SCHOOL OF CIVIL ENGINEERING

JOINT HIGHWAY RESEARCH PROJECT

JHRP-76-13

MORPHOLOGY OF THE PASTE-AGGREGATE INTERFACE VOLUME I

B. D. Barnes

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76-13

Final Report

MORPHOLOGY OF THE PASTE-AGGREGATE INTERFACE

TO: J. F. McLaughlin, Director
Joint Highway Research Project

March 16, 1976

Project: C-36-61E

FROM: H. L. Michael, Associate Director
Joint Highway Research Project

File: 5-14-5

The attached two-volume report is the Final Report on the HPR Part II Study "Fundamental Studies of Portland Cement Concrete". The title of the Report is "Morphology of the Paste-Aggregate Interface". The author is Mr. Bobby David Barnes, Graduate Instructor on our staff under the direction of Professors W. L. Dolch and Sidney Diamond.

The results of this multi-year basic research investigation provide extensive new information on the nature and morphology of the interfacial zone between cement paste and aggregate and on crack development in concrete. The information does provide a better understanding of the nature of the cement action in concrete and will be valuable in many ways for years to come.

The Final Report is submitted for acceptance as fulfillment of the objectives of the Research Study. Copies will also be forwarded to ISHC and FHWA for review, comment and similar acceptance.

Respectfully submitted,

Harold L. Michael /ms

Harold L. Michael
Associate Director

HLM:ms

cc: W. L. Dolch
R. L. Eskew
G. D. Gibson
W. H. Goetz
M. J. Gutzwiller
G. K. Hallock
D. E. Hancher
M. L. Hayes
G. A. Leonards
C. W. Lovell
R. F. Marsh
R. D. Miles
P. L. Owens
G. T. Satterly
C. F. Scholer
M. B. Scott
K. C. Sinha
L. E. Wood
E. J. Yoder
S. R. Yoder

Final Report

MORPHOLOGY OF THE PASTE-AGGREGATE INTERFACE

VOLUME I

by

Bobby David Barnes
Graduate Instructor in Research

Joint Highway Research Project

Project No.: C-36-61E

File No.: 5-14-5

Prepared as Part of an Investigation

Conducted by

Joint Highway Research Project
Engineering Experiment Station
Purdue University

in cooperation with the

Indiana State Highway Commission

and the

U.S. Department of Transportation
Federal Highway Administration

The contents of this report reflect the views of the author who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

Purdue University
West Lafayette, Indiana
March 16, 1976

TABLE OF CONTENTS

	Page
LIST OF TABLES	viii
LIST OF FIGURES (All Figures are in Volume II)	ix
LIST OF ABBREVIATIONS AND SYMBOLS	xxii
CHAPTER I - INTRODUCTION	1
1.1 Purpose of Investigation	1
1.2 Discussion of Early Morphological Investigations	2
1.3 Review of the More Recent Morphological Investigations	3
1.4 Summary of Failure, Fracture, and Composite Mechanics as Applied to Concrete	5
1.4.1 Classical Failure Theories	5
1.4.2 Fracture Mechanics of Concrete	6
1.4.3 Composite Mechanics of Concrete	7
1.4.4 Discussion of Mechanics Approaches	8
1.5 Plan of Presentation	9
1.6 Discussion of Experimental Procedure	9
1.6.1 Specimen Description	9
1.6.1.1 Type I Specimens	10
1.6.1.2 Type II Specimens	10
1.6.1.3 Type III Specimens	12
1.6.2 Equipment Used	12
1.6.3 Analytical Approach	12
CHAPTER II - EXAMINATION OF THE PASTE-GLASS INTERFACE	16
2.1 Inspection of Specimens	16
2.2 Chronological Development of the Interfacial Morphology	18
2.2.1 One-Day Specimens	20

2.2.2 Three-Day Specimens 24
2.2.3 Seven to Twenty-Eight Day Specimens 28
2.2.3.1 Morphology of the Material Removed with the Glass Substrates 28
2.2.3.2 Morphology of the Cement Paste 29
2.3 Summary and Discussion 31
2.3.1 Summary of the Morphological Development at the Interface 31
2.3.2 Separation of Paste and Substrate 33
CHAPTER III - EXAMINATION OF BULK "CONTROL" PASTES 34
3.1 Specimen Inspection 34
3.2 Comparison with Bulk Paste Morphology Observed by Others 35
3.3 Bulk vs. Interfacial Morphology 36
3.4 Spherulitic Particles 39
3.5 Summary 44
CHAPTER IV - EXAMINATION OF MORTAR SPECIMENS 45
4.1 Specimen Preparation 45
4.2 Surface Morphology of Ottawa Sand Grains 46
4.3 Comparison of Microstructures of Sand-Paste Interface in Mortars with the Glass-Paste Interfaces 48
4.3.2 Mortars of w/c = 0.50, C_v = 0.30 52
4.4 Crack Initiation and Propagation 54
4.5 Comparison of Observed Crack Patterns with Results of Previous Research 57
4.6 Summary 60
CHAPTER V - SUMMARY OF FINDINGS 62
5.1 Morphological Development of Hydration Products Near the Paste-Aggregate Interface 62
5.1.1 Microstructure at One Day 62
5.1.2 Microstructure at Three Days 63
5.1.3 Microstructure at Seven Days and Beyond 63

5.2 Crack Initiation and Propagation 63

5.3 Other Findings 64

CHAPTER VI - CONCLUSIONS 67

LIST OF REFERENCES 69

APPENDICES

Appendix I--Details of Specimen Preparation 76

Appendix II--Details of Calibration Curve Preparation 83

Appendix III--Chemical Analysis of Cements 93

Appendix IV--Raw EDXA Data 94

Appendix V--Literature Review of Failure Theories, Fracture Mechanics, and Composite Materials as Applied to Concrete Systems 106

Appendix VI--Details of Analytical Procedure for Five Micrometer Size Particles 124

Appendix VII--Figures 126

LIST OF TABLES

Table		Page
1.	Compound Composition of Cement Used by Hadley	11
2.	Compound Composition of Cements Used In Present Investigation	11
3.	Composition of Mortar Specimens (Type III)	13
4.	EDXA Analysis of Glass Slides	19
5.	Comparison of $Ca(OH)_2$ Intensity Ratios	38
6.	Possible Particle Size Distributions for a Typical Portland Cement, Based on Grindrod's Results	40
7.	Results of Analysis for SO_4^{-2} in the Minus Five Micrometer Size in Portland Cement	43
AII-1	Compounds Used in EDXA Calibration	84
AII-2	Accumulated Calibration Data	86
AV-1	Practical Formulae for Modulus of Elasticity of Concrete, Cement Mortar, and Cement Paste	116

LIST OF FIGURES

Figure (All Figures are in Volume II)		Page
1.	Calibration for CaO/SiO_2 Ratio	127
2.	Calibration for CaO/SO_3 Ratio	128
3.	Calibration for CaO/Al_2O_3	129
4.	Coding Key for Type I Specimens	130
5.	Low Magnification View of Hydration Products on Glass Substrate (A5001G1)	131
6.	Enlargement of Material on Glass Substrate (A5001G2)	131
7.	Close-up View of Grey Film Adhering to Substrate (A5001G3)	132
8.	High Magnification of C-S-H Gel Shown in Figure 7 (A5001G4)	132
9.	Low Magnification View of Hydration Products and Small Cement Grains on Glass (B5001G1)	133
10.	High Magnification Stereomicrograph of Duplex Film on Glass (B6501G2)	134
11.	Numerous Small Cement Grains Lying on Duplex Film (C5001G2)	135
12.	Duplex Film and Cement Grains on Glass (C6501G4)	135
13.	Residual Shell From an Approximately One Micrometer Diameter Cement Grain (C6501G5)	136
14.	Small Hydrated Cement Grains Exhibiting Residual Grains and Interior Voids (D5001G1)	136
15.	Sheaf-like C-S-H Gel Remaining on Glass (D5001G2)	137
16.	Enlargement of C-S-H Gel with $Ca(OH)_2$ Layer Beneath (D5001G3)	137
17.	Typical X-Ray Diffraction Pattern for a One-Day-Old Specimen (A6501G)	138
18.	Low Magnification View of Cement Paste Interface (A5001P1)	139
19.	Close-up View of On-Edge $Ca(OH)_2$ Growing Into the Paste (A5001P5)	139
20.	$Ca(OH)_2$ of the Duplex Film Adhering to the Paste (A5001P2)	140
21.	High Porosity Cement Paste with Duplex Film (B5001P1)	140
22.	Large Planar Areas of Duplex Film Adhering to Paste (C5001P1)	141

23. General View of Paste Showing Both Duplex Film and Residual Cement Grain (C6501P1) 141

24. Duplex Film Adhering to High Porosity Cement Paste (D5001P1) 142

25. Duplex Film Underlain by Linear Features Extending into the Paste (One-day-old paste made from Hadley's Cement at a 0.50 w/c) (G1B) 142

26. Early Hydration Micrograph Clearly Showing $Ca(OH)_2$ Platelets Growing in the Paste (four-hour-old paste made from Hadley's cement at a 0.50 w/c) (G 4/24 B) 143

27. One-Day-Old Paste Hydrated Beneath a Glass Slide Showing Well Developed $Ca(OH)_2$ Crystals (Hadley's Cement; w/c = 0.50) (G1C) 143

28. Spherical Residual Cement Grain and Residual Shell (A5001G6) 144

29. Interior of Residual Shell Adhering to Duplex Film (A5001G5) 144

30. Spherical Residual Cement Grain and Residual Shell (B5001G2) 145

31. Interior of Residual Shell Adhering to Duplex Film (C5001G3) 145

32. Spherical Residual Cement Grain with Residual Shell (C5001G4) 146

33. Empty Residual Hydration Shell Approximately Five Micrometers in Diameter (C6501G2) 146

34. Residual Cement Grain Inside Residual Shell with Hexagonal Platelets (C6501G3) 147

35. Residual Grain Showing Substantial Interior Void Space (D6501G4) 147

36. Hydrating Cement Grain Showing Residual Shell, Void Space, Residual Grain Morphology (A5001P4) 148

37. Rarely Observed Cement Grain Hydration Similar to Williamson's (60) Reports (A5001P3) 148

38. Hydration Similar to that Reported by Williamson (60) (A6501P7) 149

39. Apparent Inner and Outer Products of Hydration (A6501P2) 149

40. Apparently Solution Etched Cement Grain Showing Interior Void and Platelets (A6501P1) 150

41. Residual Cement Grain Retaining Contact with Residual Shell (B5001P2) 150

42. Enlargement of Cement Grain and Shell Shown in Figure 41 (B5001P3) 151

43. Relatively Smooth Residual Grain with Few Connections to Residual Shell (B6501P3) 151

44. Etched Residual Grain with Many Planar Connections to the Residual Shell (B6501P2) 152

45. Typical View of Paste Interface at One Day (C5001P3) 152

46. Enlargement of Central Residual Cement Grain Shown in Figure 45 (C5001P4) 153

47. Residual Cement Grain Having Only a Few Visible Buttressing Crystals (C6501P2) 153

48. Residual Cement Grain Exhibiting a Large Interior Void (C6501P3) 154

49. Typical View of the Paste Interface Showing an Absence of Hydrating Grains of the Type Described by Williamson (60) (D5001P2) 154

50. Enlargement of Central Cement Grain Shown in Figure 49 (D5001P3) 155

51. Typical X-Ray Diffraction Pattern for a Paste Having Little Retained Duplex Film (A6501P) 156

52. Photo-Mosaic of Paste Interface for Cement A (A5003M) 158

53. Photo-Mosaic of Paste Interface for Cement B (B5003M) 160

54. Photo-Mosaic of Paste Interface for Cement C (C5003M) 162

55. Photo-Mosaic of Paste Interface for Cement D (D5003M) 164

56. Low Magnification View of Hydration Products Adhering to the Glass Substrate at Three Days (A5003G4) 165

57. Typical Aggregation of Cement Grains Adhering to the Duplex Film (A5003G1) 165

58. Enlargement of the Aggregation Shown in Figure 57 Showing Encapsulating Lime (A5003G2) 166

59. Aggregation of Cement Grains Encapsulated by $Ca(OH)_2$ Crystals (Hadley's Cement, three days curing, w/c = 0.50) 166

60. Enlargement of Figure 59 167

61. Close-up View of Encapsulating $Ca(OH)_2$ 167

62. $Ca(OH)_2$ Crystal Attached to Duplex Film Formed on a Glass Slide Placed on Top of a 0.50 w/c Ratio Paste Cured for One Day 168

63. Close-up of Developing Duplex Film After Three Days Hydration (A500365) 168

64. Enlargement of a Region Similar to Figure 63 Showing the Changing Morphology of the C-S-H Gel (A6503G4) 169

65. Folded Over Duplex Film Probably Occurring During the Separation Process (A6503G1) 169

66. Low Magnification View of the Glass Substrate Showing Increased Removal of the Duplex Film (B5003G1) 170

67. Duplex Film Against Glass Showing Two C-S-H Gel Morphologies (B6503G5) 170

68. Enlarged View of Foreshortened C-S-H Appearing in Figure 67 (B6503G7) 171

69. Enlarged View of Rod-Like C-S-H Appearing in Figure 67 (B6503G6) 171

70. Low Magnification View of Glass Interface (C5003G1) 172

71. Enlargement of Duplex Film Appearing in Figure 70 (C5003G3) 172

72. Residual Hydration Shell with Interior Platelets Adhering to Duplex Film (C6503G1) 173

73. EDXA Analysis Appears to Indicate a Varying Thickness $Ca(OH)_2$ Layer (C6503G2) 173

74. C-S-H Gel Forming a Reticulated Network (C6503G3) 174

75. Low Magnification View of Hydration Products Adhering to Glass (D5003G1) 174

76. Additional Photograph of Hydration Products Adhering to Glass Substrate (D6503G1) 174a

77. Reticulated Network C-S-H Gel Forming (D6503G3) 174a

78. Secondary Lime Layer Forming Between the Duplex Film and Cement Paste (A5003P1) 175

79. Stereomicrograph Showing Secondary Lime and Hollow Hydration Shell (A5003P2) 176

80. Extensive Development of Secondary Lime on Cement Paste (B6503P1) 177

81. Comparison of C/S Ratio in Duplex Film and Secondary Lime (B6503P2) 177

82. Variation of C/S Ratio in Duplex Film and Secondary Lime (C6503P6) 178

83. High Magnification Stereomicrograph of Secondary Lime (C6503P7) 179

84. Hadley Grain with Residual Grain Adhering to Only One Side of the Residual Shell (C6503P8) 180

85. Duplex Film, Secondary Lime, Cement Paste Layered Structure (D6503P4) 180

86. Large Hadley Grain at Low Magnification (D6503P6) 181

87. Enlargement of Hadley Grain Shown in Figure 86 (D6503P7) 181

88. Low Magnification View of Hydration Products Remaining on Glass Substrate at Seven Days (A5007G1) 182

89. Enlargement of Duplex Film Shown in Figure 88 Showing Developing Reticulated Network Structure (A5007G5) 182
90. Duplex Film on Glass Substrate at Fourteen Days 183
91. Close-up of Duplex Film Region Shown in Figure 90 (A5014G2) 183
92. Enlargement of Duplex Film Shown in Figure 91 (A5014G1) 184
93. Glass Substrate Seemingly Devoid of Any Hydration Product by Fourteen Days (A5014G4) 184
94. Dimpled Appearance of Glass Substrate Shown in Figure 93 at Higher Magnification (A5014G5) 185
95. Alternating Light and Dark Zones Appearing on Glass Substrate at Twenty-Eight Days (A5028G1) 185
96. Dimpled Structure Retained on Twenty-Eight-Day Glass Substrate (A5028G2) 186
97. One of the Few Areas Having Retained Hydration Products on the Glass Substrate (B5007G1) 186
98. Retained Duplex Film and Hydration Shells on Glass (B5007G2) 187
99. Enlargement of C-S-H Shown in Figure 98 Showing a Rod-Like and a Foreshortened Morphology (B5007G3) 187
100. Additional Micrograph of Foreshortened and Rod-Like C-S-H Gel (B5007G5) 188
101. Extensive Development of Dimpled Structure at Fourteen Days (B5014G1) 188
102. Low Magnification of Dimpled Substrate (B5028G1) 189
103. Enlargement of Figure 102 (B5028G2) 189
104. Hydration Products Remaining on Substrate at Seven Days (C5007G4) 190
105. Seven-Day-Old Duplex Film (C5007G3) 190
106. General Morphology of Seven-Day-Old Duplex Film C-S-H (C5007G2) 191
107. High Magnification of Seven-Day-Old Rod-Like C-S-H Gel of the Duplex Film (C5007G1) 191
108. Substrate Almost Devoid of Hydration Products at Fourteen Days (C5014G3) 192
109. Peculiar Etch or Precipitation Pattern Found with Cement C at Fourteen Days (C5014G2) 192
110. High Magnification View of Figure 109 (C5014G1) 193

111. Blotchy Pattern Apparent on Substrate at Twenty-Eight Days (C5028G1) 193

112. Unidentified Particle Shown in the Center of Figure 111 (C5028G2) 194

113. High Magnification of Dimpled Substrate (C5028G3) 194

114. Scattered Hydration Products on Substrate (D5007G3) 195

115. C-S-H Gel Developed on Small Particle Remaining on Substrate (D5007G1) 195

116. Blotchy Grey Pattern on Substrate at Fourteen Days (D5014G3) 196

117. Hydration Products on Glass Substrate at Twenty-Eight Days (D5028G1) 196

118. Close-up View of Dimpled Structure Developed with Cement D (D5028G2) 197

119. Low Magnification of Cement Paste Interface Exhibiting Several "Windows" (A5007P1) 197

120. Hydration Products Overlain by Duplex Film (A5007P2) 198

121. Low Contrast View Through a Duplex Film Window (A5007P10) 198

122. High Contrast View of Figure 121 (A5007P9) 199

123. High Contrast Stereomicrograph of Fourteen-Day-Old Paste Interface (A5014P1) 200

124. High Contrast Enlargement of Figure 123 (A5014P2) 201

125. Normal Contrast Well-Focused View of Figure 124 (A5014P2) 202

126. High Contrast Photomicrograph of Blotchy Paste (A5028P3) 202

127. Cement Grains and $Ca(OH)_2$ (?) Crystal Under Duplex Film (A5028P1) 203

128. Reticulated Network Morphology of C-S-H on Cement Grains (A5028P2) 203

129. Large "Window" Appearing on Seven-Day Paste (B5007P1) 204

130. Close-up of Figure 129 Window (B5007P2) 204

131. Enlargement of Fan Shaped $Ca(OH)_2$ and Hydrating Cement Grains (B5007P3) 205

132. Composition of Blotchy Pastes Varies from the Dark to Light Areas (B5007P4) 205

133. Shrinkage Crack in Fourteen-Day-Old Paste Interface (B5014P2) 206

134. Shrinkage and Blotchy Pattern Noted on Twenty-Eight-Day Old Paste (B5028P1) 206

135.	Numerous Small Windows on Cement C Interface (C5007P1)	207
136.	Windows in Duplex Film (C5007P2)	207
137.	Rod-Like C-S-H on Cement Grains as Seen Through Duplex Window (C5007P3)	208
138.	Fourteen-Day-Old Cement Paste with No Breaks in Duplex Film (C5014P1)	208
139.	Enlarged View of Blotchy Paste Interface Shown in Figure 138 (C5014P2)	209
140.	Twenty-Eight-Day-Old Paste Interface (C5028P1)	209
141.	Few Small Windows in Seven-Day Paste Made from Cement D (D5007P1)	210
142.	Probable Ettringite Needles Immediately Underneath Duplex Film (D5007P2)	210
143.	Compositional Analysis of Cement D Paste Interface (D5007P6)	211
144.	Blotchy Fourteen-Day-Old Paste with Shrinkage Cracks Through Duplex Film (D5014P1)	211
145.	Dimpled Duplex Film on Twenty-Eight-Day Paste (D5028P1)	212
146.	Interface Region Immediately After Consolidation	213
147.	Cement Grain at Interface	214
148.	Typical Duplex Film on Substrate	215
149.	Morphology of the Interface at One Day	216
150.	Developing Microstructure at Three Days	217
151.	Cement Grain and Coating After About One Hour of Hydration	218
152.	Hadley Grain Hydration After One Day	219
153.	Close-up View of Developing Residual Shell, Void Space, Residual Grain at One Day	220
154.	Cement Grain Hydration at Three Days	221
155.	Low Magnification View of Polished Cement Control Specimen (A5003C1)	222
156.	Stereomicrograph of Polished Specimen (A5003C2)	223
157.	Air Bubble Filled by Abraded Hydration Products (A5007C1)	224
158.	Seven-Day Control Specimen Polished Transverse to the Long Axis (A5007C2)	224
159.	Enlarged View of Figure 158 (A5007C3)	225
160.	Polished Fourteen-Day Control Specimen (A5014C1)	225

161. Enlargement of Figure 160 Showing the Lack of Typical Hydration Products (A5014C2) 226

162. Low Magnification Micrograph of Twenty-Eight-Day Specimen (A5028C1) 226

163. Twenty-Eight-Day Polished Specimen Showing High Flat Zones and Irregular Subsided Areas (A5028C2) 227

164. High Flat Zones Appear to be Composed of C-S-H and $Ca(OH)_2$ (A5028C3) 227

165. Elemental Composition of Polished Control Specimen (A6501C3) 228

166. Photo-Mosaic of Fourteen-Day-Old Fractured Control Specimen (A5014F) 230

167. Photo-Mosaic of Hydration Products Just Under the Duplex Film of a Fourteen-Day Paste Interface (A5014P) 232

168. Fracture Surface of One-Day-Old Paste (A5001F7) 233

169. Hadley Grains with Portion of Fractured Residual Shell Remaining Attached (Enlargement of Grain in Lower Right of Figure 168) (A5001F5) 233

170. Fracture Surface of One-Day-Old Paste (A5001F9) 234

171. Fracture Surface of One-Day-Old Paste (A5001F10) 234

172. Hadley Grain with Residual Shell and Residual Grain (A5001F2) 235

173. Residual Shell with Only a Small Amount of Interior Residual Material (A5001F8) 235

174. Fracture Surface of Three-Day-Old Paste (A5003F1) 236

175. Higher Magnification View of Three-Day-Old Paste Fracture Surface (A5003F4) 236

176. One of a Very Few "Williamson Grains" (A5003F8) 237

177. Hadley Shell and Williamson Grain in Close Proximity (C6503F3) 237

178. Hadley Grain Showing Both Interior Platelets and Needles (A5007F1) 238

179. Empty Residual Shell (A5007F4) 238

180. Cement Grain Encapsulated by Relatively Pure Lime (A5014F1) 239

181. Close-up View of Cement Grain Shown in Figure 181 (A5014F2) 239

182. Cement Grains, Encapsulating Lime, and Empty Shells in a Twenty-Eight-Day-Old Paste Fracture Surface (A5028F1) 240

183. Stereomicrograph of Residual Shell with Interior Platelets (A6501F5) 241

184. Interior Platelets Growing on Residual Shell (A6501F6) 242

185. Lime Crystal Showing Good Cleavage Planes and Hexagonal Angles with a Few Empty Residual Shells (A651F3) 242

186. Encapsulating Lime with Void Residual Shell Beneath It (A6503F1) 243

187. Residual Shell with Smooth Interior Component (A6501F4) 243

188. Fracture Surface of Three-Day-Old Specimen (B5003F2) 244

189. Close-up View of Central Residual Shell in Figure 188 (B5003F1) 244

190. Apparent Hadley Grain and Williamson Grain Adjacent to Each Other (B5003F6) 245

191. High Magnification of Inner and Outer Product of Williamson Grain Shown in Figure 190 (B5003F7) 245

192. Fracture Surface of Three-Day-Old Paste (C5003F1) 246

193. Residual Grain Exhibiting an Extremely Clean Surface (C5003F2) 246

194. Residual Shell with Smooth Interior (C5003F3) 247

195. Lime Showing Areas of Encapsulation and Good Cleavage (C5003F4) 247

196. Fracture Surface of Three-Day-Old Paste (D5003F5) 248

197. Close-up View of Hadley Grain Appearing in the Lower Left Portion of Figure 196 (D5003F3) 248

198. Close-up View of Hadley Grain Appearing in the Center of Figure 196 (D5003F4) 249

199. Fracture Surface Showing Many Empty Residual Shells (D5003F6) 249

200. Fracture Surface Showing Residual Shells and Obvious Hadley Grain (D5003F1) 250

201. Enlargement of Hadley Grain Appearing in the Center of Figure 200 (D5003F2) 250

202. Micrograph from Diamond's Earlier Work Showing Vacant Residual Shells (w/c = 0.60, Hydrated three days) 251

203. Ottawa Sand Grains at Low Magnification (Sand--2) 251

204. Region of Smooth and Jagged Topography Occur on the Sand Grain (Sand--3) 252

205. General View of Broken Topography on Sand Grain (Sand--4) 252

206. Enlargement of Broken Topography Shown in Figure 205 (Sand--5) 253

207. High Magnification View of Broken Topographic Region (Sand--6) 253

208. Flat, Smooth, Blocky Structures with Parallel Striations (Sand--7) 254

209. Dished-out Region and Polygonal Crack Patterns (Sand--8) 254

210. Dished-out Region Appears Smooth and Polygonal Cracks Seem Deep (Sand--9) 255

211. Coding Key for Type III, Mortar, Specimens 256

212. Poorly Consolidated High Porosity, 60% Aggregate Volume Fraction Specimen (2-0.00-4) 257

213. Stereomicrograph of Fractured Mortar Surface (1-0.00-16) 258

214. Duplex Film on Flat Sand Surface (1-0.00-1) 259

215. Low Magnification View of Grain Socket (1-0.00-7) 259

216. Enlarged View of Duplex Film in Grain Socket Shown in Figure 215 (1-0.00-8) 260

217. Duplex Film Underlain by Linear Features and Exhibiting Several Windows (Figure 215 Enlargement) (1-0.00-9) 260

218. Low Magnification View of Grain Socket (1-0.00-10) 261

219. Grain Socket with Duplex Film, Secondary Lime, and Plately Crystals (Figure 218 Enlarged) (1-0.00-11) 261

220. Secondary Lime and Edge-on Crystals Appearing in Figure 218 (1-0.00-12) 262

221. Additional View of Material Underlying The Duplex Film (Figure 218 Enlargement) (1-0.00-14) 262

222. Crack at the Paste-Aggregate Interface in a Previously Unloaded Specimen (1-0.00-19) 263

223. Enlargement of Interfacial Crack in Unloaded Specimen (1-0.00-20) 263

224. Enlargement of Crack in Unloaded Specimen (1-0.00-21) 264

225. Stereomicrograph of Duplex Film on Sand Grain (1-0.30-6) 265

226. Enlargement of Duplex Film Shown in Figure 225 (1-0.30-4) 266

227. Enlargement of Duplex Film Showing the Foreshortened Nature of the C-S-H (1-0.30-5) 266

228. Stereomicrograph of Sand Grain Socket (1-0.30-9) 267

229. Undulating Duplex Film Reflecting the Topography of the Sand Grain Surface From Which It Separated (1-0.30-7) 268

230. Duplex Film Apparently Underlain by Acicular Ettringite Crystals (1-0.30-8) 268

231. Duplex Film in a Grain Socket Reflecting the Underlying Linear Features (1-0.30-2) 269

232. Enlargement of an Area Showing Underlying On-edge Crystals (Enlargement of Figure 231) 269

233. Duplex Film and Underlying Secondary Lime (1-0.30-1) 270

234. Secondary Lime Layer Appears to be Replaced by Ettringite Needles Between the Paste and Duplex Film (1-0.30-11) 270

235. Ettringite Needles Filling Interfacial Void (1-0.30-12) 271

236. Close-up View of Duplex Film on Irregular Sand Surface (1-0.30-13) 271

237. Mode of Mechanical Bonding or Interlock (1-0.30-10) 272

238. Crack Following Paste-Aggregate Interface (1-0.60-2) 272

239. Hydration Products Remaining on Sand Grain (1-0.60-3) 273

240. Low Magnification View of Sand Grain in Cement Paste (3-0.00-7) 273

241. Duplex Film on Sand Grain (3-0.00-8) 274

242. Duplex Film, Small Cement Grains, and an On-Edge Crystal on a Sand Grain Surface (3-0.00-6) 274

243. Aggregation of Cement Grains Encapsulated by Lime on a Sand Grain (3-0.00-11) 275

244. General View of Massive Lime on Duplex Film (3-0.00-4) 275

245. Enlargement of Massive Lime on Duplex Film (3-0.00-2) 276

246. Enlargement of Duplex Film and Massive Lime Contact (3-0.00-1) 276

247. Sand Grain Socket at Low Magnification (3-0.00-12) 277

248. Various Familiar Structures at Bottom of Grain Socket Shown in Figure 247 (3-0.00-13) 277

249. Secondary Lime and Lime with Good Cleavage at Bottom of Grain Socket (3-0.00-14) 278

250. High Magnification of Secondary Lime Shown in Figure 249 (3-0.00-15) 278

251. Residual Shell in Mortar Specimen Near the Aggregate Surface (3-0.00-9) 279

252. Possible Hadley Grain on Duplex Film Exhibiting a Reticulated Network C-S-H Gel (3-0.00-5) 279

253. Stereomicrograph of Sand Grain in Paste Matrix (3-0.30-4) 280

254. Hydration Products on Sand Grain (3-0.30-2) 281

255. Enlargement of Duplex Film--Aggregate Separation Shown in the Center of Figure 254. 281

256. Duplex Film with Adhering Small Cement Grains on Sand Grain (3-0.30-7) 282

257. Crack Immediately Behind the Duplex Film (3-0.30-6) 282

258. Bottom of Sand Grain Socket (3-0.30-9) 283

259. Enlargement of Figure 258 Showing Secondary Lime and Duplex Film (3-0.30-8) 283

260. Massive Lime Beginning to Separate from the Paste-Aggregate Interface (3-0.30-1) 284

261. Microcrack Propagating Around Aggregate and On Into the Paste (3-0.30-10) 284

262. Branched Crack Near the Aggregate Surface (3-0.30-11) 285

263. Microcrack Following the Aggregate Outline (3-0.60-2) 285

264. Enlarged View of Cement Grain Aggregation Shown in Figure 263 (3-0.60-1) 286

265. Small Hadley Grain on Duplex Film (3-0.60-3) 286

266. Residual Shell Near Aggregate Surface (3-0.60-4) 287

267. Residual Shells Near Aggregate Surface (3-0.60-5) 287

268. Crack Passing Between Massive Lime and Duplex Film (3-100-1) 288

269. Close-up View of Massive Lime Separation from Duplex Film (3-100-2) 288

270. Photo-Mosaic of Cracks Occurring Around a Sand Grain in a 3-0.00 Mortar 290

271. Photo-Mosaic of Cracks Occurring Around a Sand Grain in a 3-0.60 Mortar 292

272. Photo-Mosaic of Interfacial Cracks in a 1-0.00 Specimen 294

273. Photo-Mosaic of Interfacial Cracks in a 1-0.60 Specimen 296

274. Sand Grain at the Mortar-Glass Interface of a Specimen Similar to the Type I Specimen (MA3201-1) 297

275. Enlargement of Figure 274 Showing the Crack Location and Hydration Products on the Sand Grain (MA3201-3) 297

276. Interfacial Cracks Occur in Mortars Subjected to Shrinkage Only 299

277. Typical Large Crack Resulting From Unstable Crack Propagation at Failure (1-100) 301

LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Definition
C	CaO
S	SiO_2
A	Al_2O_3
F	Fe_2O_3
$\bar{S}$	SO_3
H	H_2O
M	MgO
N	Na_2O
K	K_2O
E	Young's Modulus
G	Strain energy release rate
w/c	water:cement ratio
μ	Micrometer
γ	Surface tension
ν	Poisson's Ratio

ABSTRACT

Barnes, Bobby David. Ph.D., Purdue University, December 1975. Morphology of the Paste-Aggregate Interface. Major Professor: S. Diamond.

The purpose of this research was to characterize in detail the developing morphology of the interfacial zone between cement paste and aggregate in concrete, and to assess the influence of the microstructure on the probability of crack initiation and propagation from this interfacial zone. The morphology was examined primarily by scanning electron microscopy, with chemical information on the microstructural elements being secured by an associated energy-dispersive X-ray spectrometer.

The interfacial zone was modelled by casting cement paste on clean glass microscope slides. Specimens mixed at 0.5 and at 0.65 w:c ratios were pipetted onto the slides, stored at 100% RH for eight hours, and then immersed in saturated limewater for periods ranging from 1 day to 28 days. The specimens were then gently dehydrated by continuous evacuation for three days, followed by extended storage over magnesium perchlorate $Mg(ClO_4)_2 \cdot 2H_2O$, while being protected from carbonation. Drying shrinkage resulted in the spontaneous separation of the paste from the glass slide. The two contact faces were coated with carbon and then chromium and examined in the scanning electron microscope.

It was found that duplex film of calcium hydroxide (with an apparent Ca:Si mole ratio typically around 18) formed at the interface by one day; it is believed that this initial film is oriented c-axis perpendicular to the glass. This film was either overgrown or intergrown with sheaf-like calcium silicate hydrate gel C-S-H gel particles. At one day almost all of the film remained with the glass on separation, little of it being found with the paste. Typically the film carried with it large aggregations of cement grains which in turn were engulfed by large crystals of impure calcium hydroxide. These crystals were highly substituted hexagonal plates approximately one

micrometer thick and thirty to fifty micrometers on a side. Elemental analysis revealed apparent Ca:Si ratios of from 3 to 10. These crystals attached themselves to the duplex film by either growing directly from the initial lime film or by engulfing the duplex C-S-H gel.

Sometime between two and three days a secondary layer of about a micrometer thickness began forming over and parallel to the duplex film initially laid down at the interface. This secondary layer appeared to be exceedingly pure calcium hydroxide (apparent Ca:Si ratio of the order of 60). It continued its growth with increasing time of hydration and thereby tended to tie the initial duplex film to the bulk paste. By 3 days hydration, this effect resulted in roughly 50 percent of the areal extent of the film remaining with the paste on separation, the other half continuing to adhere to the glass slide. There was evidence of much fracture between the original duplex film and this secondary calcium hydroxide layer. By seven days the amount of this fracture decreased to negligible proportions, and instead the fracture at the spontaneous separation appeared to undulate from the glass into the original lime layer of the duplex film. The bulk of the film went with the cement paste on separation, and "windows" through which to observe the microstructure of the interior on the paste side became increasingly difficult to find. This type of fracture continued for specimens exposed to hydration for 14 and for 28 days.

Furthermore a peculiar mode of hydration resulting in the appearance of a void space between the outer portion of hydrating cement grains and their unhydrated cores was observed. This mode of hydration appeared both at the interface and in the bulk paste.

In general, similar phenomena were observed in silica sand mortars.

NOMENCLATURE

It is common practice in the cement industry and among those engaged in research relating to portland cement and concrete, to report analytical data on the basis of oxides of the elements present. Abbreviations for the more common oxides have been developed and are universally used in the literature. The common oxides and their abbreviations are listed below.

COMMON OXIDES AND THEIR ABBREVIATIONS

Oxide	Abbreviation
CaO	C
SiO_2	S
Al_2O_3	A
Fe_2O_3	F
SO_3	$\overline{S}$
H_2O	H
MgO	M
Na_2O	N
K_2O	K

The major phases present in portland cement are commonly referred to in terms of combinations of the abbreviations for their constituent oxides. Tricalcium silicate ($3\ CaO \cdot SiO_2$), for example, would be called C_3S. The substituted forms of the anhydrous phases actually present in cement have also been given so called "mineral" names. Thus impure C_3S is called "alite". The abbreviations and "mineral" names for the principal cement compounds are listed in Table 2.

TABLE 2

NOMENCLATURE AND ABBREVIATIONS FOR MAJOR CEMENT COMPOUNDS

Chemical Composition	Abbreviation	"Mineral" Name
$3CaO \cdot SiO_2$	C_3S	Alite
$2CaO \cdot SiO_2$	C_2S	Belite
$3CaO \cdot Al_2O_3$	C_3A	Aluminate phase
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ *	C_4AF	Ferrite phase

* actually solid solution series ranging roughly from C_2F to C_6A_2F.

A relatively complex system of nomenclature has also been developed for the hydration products of portland cement. A brief description of the principal hydration products and their nomenclature is given below:

Lime: One of the principal products of cement hydration is calcium hydroxide, which is normally referred to as lime. The mineral name, portlandite, is also sometimes used.

C-S-H gel: Both silicate phases in cement hydrate to produce a poorly-crystallized and highly-substituted material referred to as calcium silicate hydrate gel. This material has a non-stoichiometric composition and an extremely high surface area. The x-ray diffraction pattern exhibits three broad peaks that correspond to the principal peaks for the mineral tobermorite. For this reason, some authors have referred to it as "tobermorite gel".

The designation currently accepted is the hyphenated form, C-S-H gel, the hyphens being used to convey the variable composition.

Sulfoaluminates: During early hydration, the aluminate phase in portland cement reacts with sulfate ion released from the gypsum added to cement to control the rate of hardening. The hydrated calcium aluminate sulfate that forms is of two types. The first formed product has the composition $C_3A \cdot 3\ \overline{CS} \cdot H_{32}$, and is called ettringite.

The second form, which is produced by reaction of the ettringite with additional aluminate released by the hydrating C_3A, has the composition $C_3A \cdot \overline{CS} \cdot H_{12}$ and is referred to as monosulfoaluminate or more properly, tricalcium aluminate monosulfate-12-hydrate.

CHAPTER I - INTRODUCTION

1.1 Purpose of Investigation

Portland cement concrete is perhaps the most extensively used manufactured construction material. Its use may be dated to the early nineteenth century; since then, the volume used in the construction industry has increased each year. Research in the nineteenth and twentieth centuries has led to considerable improvement in the material, especially with respect to its compressive strength. As late as about 1910 a compressive strength of 750 psi was considered extraordinarily high (1); today compressive strength design values range from a typical 3500 psi to an occasional 10,000 psi.

Much of the improvement in concrete quality has come about as the result of better understanding of the chemical and mechanical aspects of the material. Unfortunately chemists and engineers engaged in generating improvements usually have worked separately. Typically chemists have been interested in the chemical reactions occurring in the cement paste and between the paste and aggregate in the concrete, whereas engineers have been concerned principally with the macro-properties of the material e.g., its strength, elastic modulus, and stress-strain behavior. Only recently have these two disciplines communicated their findings to each other. A common concern has been expressed regarding the presence, initiation, and propagation of microcracks (small cracks near the paste-aggregate interface) which seem to influence the performance of concrete systems significantly.

Evidence of the need and the desire for better understanding of this aspect of the interrelationship between chemical and mechanical behavior of portland cement concrete is apparent from the Proceedings of the International Conference on the Structure of Concrete (2) held in 1965. Therein authors from several disciplines expressed their opinions and discussed research findings concerning the behavior of

concrete under load. Many of the reports presented suggest that microcracks significantly influence creep, fatigue, and strength of concrete (1).

Since 1965 interest in the relationship between microcracking and portland cement concrete strength has continued. However, until recently little attempt has been made to relate microcracking to the microstructure of portland cement concrete. The present investigation is based on the realization that an important relationship might exist between the structure and morphology of the paste-aggregate interface and the initiation and propagation of microcracks that lead to eventual failure.

The purpose of this investigation is twofold:

1. to characterize, in detail, the developing morphology of the interfacial zone between cement paste and aggregate in concrete, and
2. to assess the influence of the microstructure on crack initiation and propagation from this interfacial zone.

1.2 Discussion of Early Morphological Investigations

While interest in the contact zone between portland cement and aggregates has existed for some time (3), current research can be said to have begun with Farran's (4) work published in 1956. Using light microscopy and X-ray diffraction, Farran investigated the contact zone developed between various types of cement and several aggregates. Cements investigated included portland cement, portland-blast furnace slag cement, high alumina cement, and supersulfated cement. Aggregates studied included calcite, dolomite, quartz, flint, feldspar, mica, and glass (in the form of microscope slides).

Farran's findings with respect to portland and portland-blast furnace slag cement, which bear most closely on this study, were as follows:

1. "In a portland cement concrete (and to some extent a portland-blast furnace slag cement) the contact between the cement and the embedded materials is essentially secured by portlandite* crystals, often accompanied by gel."

*Portlandite, lime, and $Ca(OH)_2$ are used as synonyms describing the same compound in this text.

2. No epitactic bond between $Ca(OH)_2$ precipitated from the paste and aggregates other than calcite was observed.
3. The bond strength between paste and aggregate was significantly diminished (often zero) when the paste and aggregate were allowed to dry.

Microscopic research dealing with the paste-aggregate interface was continued and refined by later workers (5-18). A consensus of the results of these investigations can be expressed in the following observations:

1. Cracks originate near the paste-aggregate interface.
2. As concrete is subjected to increased stress these interfacial cracks elongate, join together, and eventually traverse the concrete, causing failure.
3. The "disturbed" or "interfacial" zone surrounding the aggregate particles ranges from approximately 30 to perhaps 200 micrometers.

Although the authors cited above generally agree that cracks initiate near the interface at least with coarse aggregate, there is some disagreement as to the origin of these cracks. The work of Farran (4) and the observations and calculations of Slate and Hsu (8) seem to indicate that in dry mortars and concretes, the cracks are initiated as a result of drying shrinkage. However, Hansen (13) using samples dried several years, reported that no drying shrinkage cracks were present.

1.3 Review of the More Recent Morphological Investigations

More recent work associated with the paste-aggregate interface has been presented by Farran et. al. (19), Hadley (20), Schmittgrund et. al. (21), and Javelas et. al. (22). The research of Farran et. al. and Javelas et. al. made use of transmission electron microscopy. These workers were successful in the production of thin specimens by ion etching, examination of which revealed aspects of both the aggregate and cement paste near the original interface. However, it has been difficult to evaluate the structure of the interfacial zone from their

published results, except that their work does support the concept of an "aureole de transition" (19) about the aggregate-paste interface.

Hadley (20) and Schmittgrund (21) chose to use scanning electron microscopy (SEM) in their investigations. The results of these authors support the proposition that cracking does initiate and propagate near the original paste aggregate interface. Perhaps the more enlightening results stem from Hadley's work, which both supports and extends the early results of Farran (4). For portland cement paste in contact with aggregate surfaces, these results may be briefly stated as follows:

1. On the aggregate surface a layer of $Ca(OH)_2$ is precipitated with its c-axis preferentially oriented perpendicular to the aggregate interface. This portlandite layer ranges from 0.25 to 0.50 micrometers in thickness.
2. Immediately above the $Ca(OH)_2$ layer (i.e. toward the paste) C-S-H gel begins to grow forming a combined or "duplex" film. The two layers taken together typically are about one micrometer in thickness.
3. As hydration proceeds, the initial $Ca(OH)_2$—C-S-H duplex film is bound to the bulk paste by the growth of large impure $Ca(OH)_2$ crystals growing roughly c-axis parallel to the aggregate surface.
4. Cement grains near the aggregate surface appear to hydrate by a through-solution process resulting in the production of hollow "hydration shells." This implies that a porous zone may develop near the interface as a consequence of the presence of these empty hydration shells.
5. These shells were thought to be composed of $Ca(OH)_2$ platelets oriented with their c-axis roughly perpendicular to the aggregate surface.
6. Interfacial cracks develop either below or above the duplex film or within the bulk paste, depending upon the length of hydration and the type of aggregate.

Most of Hadley's conclusions have been substantiated in the present research. However, there are several discrepancies which will be discussed subsequently.

1.4 Summary of Failure, Fracture, and Composite Mechanics as Applied to Concrete[1]

1.4.1 Classical Failure Theories

Perhaps the most extensive comparison of classical failure theories with actual load-induced failure conditions was presented by Robinson (11), who listed at least seven different failure theories, viz:

1. maximum principal stress theory
2. maximum principal strain theory
3. maximum shear stress theory
4. internal stress theory
5. Mohr's theory
6. octahedral shear stress theory, and
7. strain energy theories.

All of the above theories are based upon the assumptions that the material being analyzed is homogeneous, isotropic, and elastic up to some critical stress predicted by the theory. Usually this critical stress was taken as the elastic limit.

Investigations of suitability of these theories as predictors of failure in concrete required that they be analyzed against concrete strength data. To do this Robinson assembled previously published strength data from a variety of sources, including Richart, Brandtzaeg, and Brown (23), Balmer (24), Bellamy (25), Wastlund (26), Wiegler and Becker (27, 28), McHenry and Karni (29), Bresler and Pister (30, 31), and Tsuboi and Suenaga (32). This data consisted of the strength results from a total of 516 specimens made from 43 concrete mixes. After considerable analysis Robinson concluded that no single failure theory adequately described the failure of concrete either quantitatively or qualitatively (11).

[1] A more exhaustive literature review of this topic is provided in Appendix V.

1.4.2 Fracture Mechanics of Concrete

Beginning in the early nineteen sixties and continuing into the nineteen seventies much interest has been expressed in the application of fracture mechanics to cement and concrete systems (33-38). The research conducted in this area has sought to apply the theories of Griffith (39) and Irwin (40) to concrete cracking leading to failure. These theories suggest that there exists a direct relationship between the strain energy stored in a material and the energy required for the production of new surface as a result of crack initiation or propagation.

The research has followed many different approaches. Often the Irwin, Griffith, and Inglis (41) theories have been interchanged and interrelated primarily through the use of K, the stress intensity factor. Much of this work has been disappointing. The obvious reason for this disappointment is that concrete does not meet the assumptions of these theories. It is not homogeneous, elastic, isotropic, or continuous. Even with these shortcomings a useful characterization of a particular concrete mix might be obtainable if only one of the three approaches mentioned were used. However, researchers have tried to equate the three approaches using the K factor. It does not seem reasonable that one should be able to relate three theories which are based on linear elasticity with a material which at the phenomenological level is non-elastic and non-linear in response to load.

Notwithstanding, Naus et. al. (37) and Glucklich (33, 34) have made progress in the qualitative use of fracture mechanics. Naus et. al. evaluating K_c' (a critical stress intensity factor for a particular concrete) for various concrete mix proportions concluded that:

> "varying the coarse aggregate content or gradation of coarse aggregate, or type of coarse aggregate" can influence the resistance to crack propagation in concretes (37).

In addition several figures were published showing the relationship of various mix properties to K_c', which might prove helpful from a design point of view.

Glucklich (33) working with concrete in compression has contributed much to the application of fracture mechanics to concrete. In his research he has illustrated that no critical size flaw may exist in a compression field. Indeed he argues that crack propagation to failure in concrete is a stepwise function consisting of at least two phases--slow crack growth and rapid crack growth. Additionally he points out that concrete in conventional compression is subjected to shear and to dynamic loading as a result of the end restraint of the compression specimen and as a result of the rapid release of stored energy in the testing machine.

1.4.3 Composite Mechanics of Concrete

Little work other than that reported by Feret (3) in 1897 and that of Abrams (42), Wischers (43), and Powers (44) in the early to middle 1900's has dealt with the strength of concrete from a composite mechanics point of view. Typically this older work was empirical and phenomenological in character. A recollection of Abrams' research shows the following relationship:

$$S = A/B^{x}$$

where: S = compressive strength at 28 days

A = 14,000 psi

B = 7

x = water/cement ratio by volume

In contrast to the limited composite strength research available there exists a substantial amount of work related to the composite elastic modulus and the composite bulk modulus. The most interesting work stems from the mathematical analyses of particulate systems of Brandt (45) and Brown (46). This research has sought to compare concrete to particulate systems having full and zero continuity. The extensive mathematical models which result from these analyses are almost untractable. In addition none of this work appears to consider either tensile forces or possible discontinuities. Consequently Mather (47) doubts that these models represent even a facsimile of "Prepakt" concrete.

Hansen (48) after making an apparently thorough review of the literature has suggested that composite systems approximating the characteristics of concrete may be of two types:

1. high modulus matrix with low modulus particles and,
2. low modulus matrix with high modulus particles

Using the values of -1.0 and +0.5 for Poisson's ratio in composite mechanic equations suggested by Hashin (49), Hansen has shown that

$$\text{for } \nu = -1.0; \quad E = (1-g)\, E_m + gE_p$$

and for;

$$\nu = +0.50, \quad E = 1/\left(\frac{1-g}{E_m} + \frac{g}{E_p}\right)$$

where: E = Young's modulus

g = fractional volume of particles

E_m = matrix modulus

E_p = particle modulus

Even though these formulae somewhat approximate the moduli of concrete, it seems somewhat unreasonable to use values of Poisson's ratio which significantly vary from the normally accepted value of 0.16.

1.4.4 Discussion of Mechanics Approaches

Several approaches have been used in efforts to predict concrete strength and elastic modulus. All of these depend upon the theory of elasticity and the material's reaction to load on a phenomenological level as their basis. No theory appears to suitably represent the reaction of concrete to load at least under complex states of stress.

There appears to have been a general disregard for the micro-structural features in the theories presented to date, although a few authors make reference to Brunauer's work (50) (and the model of cement paste suggested therefrom). In the end suitable formulations for the prediction of the reaction of concrete to load may be established only when significant experience has been accumulated for a given mix. At this time there does not seem to be any readily available reservoir of theory to allow the rational modelling of concrete systems.

1.5 Plan of Presentation

The thesis is presented in the following sequence. Immediately following this section a discussion of the experimental procedure is presented, which will briefly acquaint the reader with the tools, techniques, and rationale adopted during the investigation.

In Chapter II, Analysis of the Paste-Glass Interface, the results of morphological and X-ray diffraction investigation of the interfaces between glass slides and portland cement pastes are presented. The paste-aggregate interface is treated in an idealized and therefore simplified manner. The sequence of presentation follows the time of hydration.

In Chapter III, Analysis of Control Pastes, the necessity of comparing interfacial morphologies to those structures occurring in bulk paste is discussed, and such comparisons are made in detail. It will be noted in this chapter that all known techniques of specimen preparation may introduce significant artifacts.

In Chapter IV, Analysis of Mortar Specimens, investigations are reported on the influence of water-cement (w/c) ratio, volume fraction of sand (C_v), and stress level, on the initiation and propagation of interfacial cracks. A prominent feature of Chapter IV is a detailed comparison of interfacial morphological features found at interfaces between paste and glass slides with corresponding features found at paste-aggregate interfaces in mortars.

In Chapter V all of the results are drawn together to present a concerted picture of the morphology of the paste-aggregate interface and its influence on crack propagation behavior.

1.6 Discussion of Experimental Procedure

1.6.1 Specimen Description

Details of the specimen preparation processes are provided in Appendix I. Basically three types of specimens have been used:

I. cement pastes cast against horizontal glass microscope slides,

II. cement pastes from the same batches prepared for Type I specimens, but cast in roughly 2.54 cm x 10 cm cylindrical

polyethylene centrifuge tubes. These specimens are referred to as the "control" specimens.

III. mortar specimens cast in a manner similar to Type II paste specimens. Pure silica sand as specified in A.S.T.M. Designation: C-103 was used as the aggregate.

1.6.1.1 Type I Specimens

During Hadley's (20) preliminary research it was confirmed that similar morphologies occurred at the interface with various aggregates including quartz, calcite, galena, orthoclase, etc. However, Hadley used only a single portland cement, the composition of which is given in Table I.

One objective of the present study has been to evaluate the generality of those results. Four different kinds of cement were used in the present research: (a) a high alkali Type I portland cement, (b) a low alkali Type I portland cement, (c) a Type IS portland-blast furnace slag cement, and (d) a Type V portland cement. Table 2 presents the compound compositions of these cements. Specimens were prepared from each of the cements at w/c ratios of 0.50 and of 0.65. Curing times of 1, 3, 7, 14, and 28 days were used. At the conclusion of the designated curing period, hydration was stopped by continuously evacuating the specimens for three days through a liquid nitrogen trap, and then by storing in vacuum over $Mg(ClO_4)_2 \cdot 2H_2O$ for a minimum of two weeks.

1.6.1.2 Type II Specimens

Type II specimens of pastes cast in cylinder form were prepared concurrently with the Type I specimens. The same variables of cement composition, of w/c ratio, and of curing time were used, and these specimens were dried concurrently with the Type I specimens. Both fractured surfaces and polished surfaces of the bulk paste were examined. All fracture surfaces and polished surfaces were transverse to the long axis of the cylinders and were positioned at about mid-height.

TABLE 1

Compound Composition of Cement Used by Hadley (20)

Type	C_3S	C_2S	C_3A	C_4AF	Total Alkalies, (Na_2O)
I	51.20	23.83	11.00	5.99	0.38

TABLE 2

Compound Composition of Cements Used in Present Investigation

Cement	Type	C_3S	C_2S	C_3A	C_4AF	Total Alkalies (Na_2O)
A	I	48.82	22.82	9.27	9.18	0.69
B	I	64.62	11.04	9.13	7.53	0.31
C*	IS	55.19	19.17	9.54	8.36	0.08
D	V	60.83	19.10	4.51	8.60	0.37

*Composition of the 65% portland cement component

1.6.1.3 Type III Specimens

Mortar specimens were prepared using the "A" (high alkali, Type I) cement only. The w/c ratios, aggregate volume fractions used are shown in Table 3. Specimens were all cured for two weeks, dried for three days by continuous evacuation, and then mechanically loaded to 0%, 30%, 60%, or 100% of their ultimate compressive strength. After loading, the specimens were fractured transversely using a hammer and chisel. While awaiting SEM analysis these were stored over $Mg(ClO_4)_2 \cdot 2H_2O$.

1.6.2 Equipment Used

The primary tool used in the analysis was a JEOLCO SMU-3 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Sectrometer (EDXA) manufactured by Nuclear Diodes, Inc. Additional equipment included:

1. A General Electric XRD-5 X-ray diffractometer equipped with a high intensity copper tube for X-ray diffraction analysis;
2. A Beckman IR-10 Infra-Red Spectrophotometer for determination of carbonation effects;
3. A Baldwin 120,000 pound universal hydraulic testing machine for loading the cylindrical mortar specimens;
4. A gloved box continuously flushed with N_2 to provide a CO_2-free atmosphere for specimen preparation; and
5. A Data General Nova 1200 computer equipped with an EDIT/1/707 computer program prepared by Nuclear Diodes, Inc. for manipulation of the EDXA data.

1.6.3 Analytical Approach

Specimens of Types I and II were used to compare paste-aggregate interfacial hydration morphology with bulk paste hydration morphology. The Type III specimens served both as a simplified model of concrete and as an assurance that the Type I specimens provided features analogous to those of true paste-aggregate interfaces. While it appears that some saving of effort may have been realized by using Type III specimens

TABLE 3

Composition of Mortar Specimens* (Type III)

Mix Number	W/C	Volume fraction of Sand (C_v)
1	0.32	0.30
2	0.32	0.60
3	0.50	0.30
4	0.50	0.60

*All specimens were made with cement "A" and cured for two weeks.

only, the Type I specimens were far more suitable in geometry for both SEM and X-ray diffraction analysis.

The Type I specimens allowed both the paste side and the aggregate side of the interface to be observed separately over large areas. Normally the separation between paste and glass occurred spontaneously near the original paste-glass interface as the result of significant drying shrinkage strains in the weak interfacial zone. Once the two sides of the interface had separated, they were individually used for X-ray diffraction and/or SEM analysis. The only special procedure required in this analysis was the coating of the two interface components with a conducting layer of chromium over carbon for the SEM work. Thus statements concerning the morphology and the fractography of the interface could be made with little concern for the possible effects resulting from specimen preparation.

Without the Type II (control) specimens no conclusive statements could be made to compare bulk paste hydration (i.e. hydration removed from an aggregate surface) with interfacial hydration. Two procedures were investigated for the preparation of these specimens. One process involved the use of fracture surfaces; the other polished surfaces. Some difficulty was encountered with the polished surfaces, and fracture surfaces, being considered the best available specimens for examination, were accordingly used. The details of this difficulty are discussed in Chapter III.

As mentioned above the Type III specimens were also used as a type of control specimen, i.e. to assure that the Type I results accurately duplicated the true paste-aggregate interface. Additionally these specimens were subjected to compression in several different ranges of stress, to permit evaluation of the crack initiation-propagation sequence. The w/c ratios were chosen for specific reasons. The 0.50 w/c ratio provided specimens which allowed the individual morphological features to be clearly isolated and examined within the microscope, while specimens made at a w/c ratio of 0.32 exhibited less detail of individual

morphological features, but showed a more readily delineated crack pattern for fracture analysis.

The procedures chosen provided for the accurate modelling of the paste-aggregate interface and for appropriate evaluation of the crack initiation-propagation phenomena.

CHAPTER II - EXAMINATION OF THE PASTE-GLASS INTERFACE

2.1 Inspection of Specimens

The specimens used in this phase of the investigation were prepared by casting cement pastes of types, w/c ratios, and ages as described in section 1.6.1.1 against horizontally positioned microscope slides. The slides were of soda-lime glass with dimensions of 27 x 46 x 1.2 mm. The total thickness of the slide plus the overlying paste varied from 5 to 8 mm. As noted earlier the two components of the specimen, paste and glass, separated spontaneously on drying, thus providing convenient specimens for both SEM and X-ray diffraction analysis. Glass microscope slides were chosen in lieu of mineral substrates primarily because of the ease of preparation. However, it should be noted that Hadley (20) previously confirmed that the same general morphology developed independent of the nature of the substrate.

The paste and the glass were placed in separate polyvinylchloride bags after drying to protect them from moisture and CO_2 contamination. They were then removed to the diffractometer for analysis, which was carried out through the bag. When the X-ray analysis was completed, the specimens were taken from their plastic bags, broken to a convenient size, and mounted on aluminum SEM stubs. Subsequently they were coated with a thin film (200 to 500 Å thick) of chromium over carbon to prevent charging in the SEM.

Prior to any specimen analysis, several glass slides were analyzed using both the diffractometer and the SEM. As would be expected the glass showed only an amorphous X-ray diffraction pattern. Typically the slides appeared demonstratably flat and clean in the SEM for magnifications of up to 30,000X. EDXA analysis of the glass slides indicated the presence of sodium, magnesium, silicon, potassium, and calcium with some traces of iron and manganese. Tabulated results of the EDXA analysis are presented later in this section.

The availability of an energy dispersive X-ray spectrometer in combination with the SEM used in this study provided a unique ability to analyze morphology and to estimate the stoichiometry of the components of interest. A complete discussion of the equipment and techniques is somewhat outside the scope of this presentation, and the reader is referred to Russ (51) and Diamond (52-54) for details. However, a short description taken from the paper by Diamond is quoted below:

> "Briefly, the device functions to detect, count, and allocate to energy classes the X-rays produced from a small region of the specimen selected for analysis. When used in conjunction with the SEM the detector takes the form of a cryogenically-cooled silicon device mounted in the SEM sample chamber near the specimen. When the electron beam is focused on the area of interest, X-ray photons generated by the sample interact with this silicon detector to produce electrical pulses that are proportional in height to the energies of the photons. A multichannel analyzer is used to sort the pulses into narrow individual energy ranges ("channels"), and to accumulate the count of pulses assigned to each channel. Equipment is provided to record and display the resulting distribution of counts vs. X-ray photon energy. The chemical elements present in the area examined are readily identified by reference to their characteristic X-ray spectra. The K lines are readily observed for most of the elements of interest in hydrated cements, except for a few heavy elements for which L lines may be used. Commercial systems using thin windows can readily detect elements as low as Na (atomic number 11). The spectra are displayed continuously on a cathode ray tube while being accumulated, and after completion of the counting the data may be read out numerically on a teletypewriter, plotted graphically on an x-y recorder, or transmitted directly or indirectly to a computer for further processing." (53)

Using the EDXA equipment, it has been possible to construct calibration curves (53) allowing the estimation of molecular compositions (on a ratio basis) of structures observed with the SEM. The calibration curves used in this research are presented in Figures 1, 2, and 3. It should be noted that elemental analyses are reported herein on the basis of oxides rather than elementary composition. Therefore the usual abbreviations for the oxides commonly occurring in cements are

used, and are included in the list of "Abbreviations Used" at the beginning of the text. Appendix II presents the details concerning the derivation of the calibration curves. The EDXA data obtained during this investigation was secured by:

1. affixing the electron beam upon the spot (or in some cases the area) for which an elemental analysis was desired;
2. allowing the multichannel analyzer to accumulate 100,000 counts over a range of 0-8 KeV;
3. using the Nova 1200 mini-computer and the EDIT/1/707 computer program to subtract the background; and
4. having the integrated peak intensity printed from the computer memory.

Later the Ca/Si, Ca/Al, and Ca/S K-α count ratios were calculated and the molecular ratios determined from the calibration curve equations. Typically, 50,000 to 75,000 counts remained after the background was subtracted. Occasionally the rate of accumulation of counts was unusually slow. In all cases where the count rate was slower than about 300 to 400 counts per second, the EDXA analysis was terminated, since it was assumed that the feature of interest was in some way obscured from the detector. The EDXA analysis for five of the glass slides is presented in Table 4.

2.2 Chronological Development of the Interfacial Morphology

The development of the morphology at the paste-glass interface is a time-dependent process. A rather large number of examinations and microphotographs are required to properly document this developmental process. Because of this feature of the investigation it is desirable to systematize the discussion of the evidence and adhere to a definite sequence of discussion.

It was observed that most of the detectable changes in the interfacial morphology occurred during the first three days of hydration. In consequence, the discussion of the developing features is given in the following sequence: (a) one-day specimens, (b) three-day specimens, and (c) "mature" specimens varying in age from seven to twenty-eight days.

TABLE 4

EDXA Analysis of Glass Slides

Specimen No.	Counts Remaining[1]	Na[2] 1.05[3]	Mg 1.27	Al 1.51	Si 1.76	S 2.32	K 3.32	Ca 3.71	Mn 5.89	Fe 6.40	C/S[4]	C/A[5]
1	55,696	931	320	---	44,402	---	412	6921	---	---	0.16	---
2	60,087	779	296	1056	44,579	32	568	7298	---	82	0.16	6.91
3	60,092	842	382	---	44,755	---	434	7254	132	---	0.16	---
4	61,046	915	416	1769	45,115	36	432	7176	150	24	0.16	4.06
5	61,004	856	388	2062	45,022	32	451	7270	---	---	0.16	3.53

[1]Counts Remaining After Background Substraction

[2]Element Detected

[3]Approximate Location of KΩ X-rays in KeV

[4]CaO/SiO_2 Molar Ratio

[5]CaO/Al_2O_3 Molar Ratio

The format used varies slightly depending on the age of the specimen considered. In Section 2.2.1 the observations on one-day-old specimens are discussed, first in terms of observations on the glass side for specimens of all of the cement types used, and then in terms of observations on the individual pastes. A similar pattern was followed in Section 2.2.2 for three-day-old specimens. For discussion of the mature specimens in Section 2.2.3 the presentation was altered slightly; here all the 7, 14, and 28 day glass specimens were considered and then all the companion paste specimens.

Most all of the photomicrographs discussed in the above sections are from the 0.50 w/c composition specimens. A few 0.65 w/c composition specimens are shown when that photograph better represents a particular phenomenon than the existing photograph of the companion 0.50 w/c composition specimen. One of the conclusions of this investigation is that both the 0.50 w/c and 0.65 w/c compositions develop the same structure at their interface, at least during the hydration period studied.

Before proceeding to the individual descriptions of the results, it is urged that the reader study Figure 4, Coding Key for Type I Specimens. Failure to become thoroughly familiar with the specimen coding will result in considerable difficulty in identifying the specimens and understanding their morphology.

2.2.1 One-Day Specimens

Figures 5 and 6 show the hydration products deposited on the glass substrate by a high alkali Type I cement prepared at a w/c ratio of 0.50. Large numbers of hydrating single cement grains may be seen adhering to the grey areas on these slides. Closer views of the grey zones are provided in Figures 7 and 8. The rod-like shape of this material implies that it is probably C-S-H gel (16, 17, 52, 53, 55, 56). Figures 9 through 16 provide additional views at various magnifications of other glass substrates from specimens of the other cements at both w/c ratios. The exact identification of each specimen is provided in the coded designation at the end of the figure title. One should

especially note the large number of open or empty shells lying on the surface of the C-S-H gel layer. Figures 9, 11, 12, 13, and 14 show these well. The stereo-micrograph shown in Figure 10 allows detailed analysis of the grey film deposited on the glass substrate. The black zone in the lower left is the glass substrate itself. This substrate is overlain by a two-component film. The lower layer seems to be relatively continuous and has either been overgrown or intergrown with rod-like C-S-H gel. Judging from this micrograph and others of a similar nature the grey zones deposited on the glass consist of a "duplex film" believed to be $Ca(OH)_2$ at the base with C-S-H gel above. Typically the total thickness of this film varies from 1.0 to 1.5 micrometers. The results of EDXA analyses from Figures 7, 8, and 16 are unfortunately of little help in the determination of the composition of the interfacial material on the glass substrate, because the X-rays given off by the specimen not only come from the particular feature of interest but from underlying and closely surrounding material (54). Generally the electron beam causes radiation from an area up to several micrometers in diameter and of about the same depth. Therefore, when dealing with substances deposited on the glass, it should be recalled that the glass itself supplies large numbers of Si X-rays that strongly influence the analysis. This problem will persist throughout the investigation.

In order to substantiate the supposition that the material deposited directly on the glass at the interface was $Ca(OH)_2$, X-ray diffraction patterns of the one-day glass substrates were evaluated. These diffraction patterns confirmed that the base of the duplex film was composed of $Ca(OH)_2$. In addition it was noted that the peak height intensity ratio for the 001 peak to the 101 peak was generally 1.5 to 3.0 instead of the value of 0.74 listed for randomly oriented $Ca(OH)_2$ powders in the A.S.T.M. X-ray Powder Data File (No. 4-0733 (57)). Since the present patterns were derived from the "bag specimens" which resulted in low intensities, it was decided to evaluate the glass substrate in air.

A typical diffraction pattern, for a specimen coded A6501G (cement A, 0.65 w/c, 1 day old, glass side) is reproduced in Figure 17. The intensities, while low because of the extreme thinness of the $Ca(OH)_2$ layer, are quite reproducible. As a result of these X-ray diffraction results, it appears that the $Ca(OH)_2$ on the glass substrate is preferentially (but not perfectly) oriented with the c-axis perpendicular to the glass. It was not possible to confirm the presence of C-S-H gel in the duplex film from the X-ray diffraction pattern. This is not surprising as C-S-H gel yields only a diffuse diffraction pattern which is not easily identified (58).

As alluded to above, the black areas on the substrate are areas of clean glass. What appear to be morphologically similar black zones are readily noted when examining the companion paste specimens, Figures 18-24. EDXA analysis given in Figures 19, 20, and 23 reveal C/S molar ratios ranging from 12 to 47 for these black zones on paste specimens. This indicates that most of these are areas of $Ca(OH)_2$, possibly with some substitutional impurities. The $Ca(OH)_2$ layer mirrors the smooth surface of the glass on which it was originally deposited. The areas that came away with the paste were formerly joined to the overlying paste in some manner and separated from the glass when the specimen dried. Many of these flat, black zones appear to be attached to elongated features which extend into the paste, for example that shown in Figure 25. Figure 26, a micrograph at an early hydration stage (four hours), shows a region where the $Ca(OH)_2$ layer has pulled away with the glass, leaving the overlying paste structure exposed. The elongated features which seem to be just underneath the $Ca(OH)_2$ layers of duplex film shown in Figure 25 are now exposed. They seem to be relatively pure hexagonal crystals having a high C/S molar ratio. Additional information is available in Figure 27. This specimen was prepared by placing the glass slide above the paste. As hydration proceeded, "bleed water" accumulated under the glass creating a free space in which crystals could grow. From their hexagonal shape and high Ca content these crystals are clearly

$Ca(OH)_2$. The foregoing would therefore suggest that $Ca(OH)_2$ may grow in the paste, extend down (or up, as in this case) to the C-S-H gel, and become bonded to the duplex film. As will be shown later, these crystals may or may not pull the duplex film with them when the substrate and paste separate.

An additional feature worthy of note is exhibited in Figures 14, 19, 20, 21, and 23. Close inspection shows the occurrence of many cement particles which have pulled apart in the plane of the interface. Several of these are clearly empty while others contain what are thought to be residual cement grains. A significant feature of those with residual grains is the void space separating the outer shell from the residual grain.

Many cement particles exhibiting this residual shell, void space, residual grain morphology have been analyzed for morphology and elemental composition. Figures 28-50 give a reasonable idea of the variability of these structures. Figures 28, 30, and 32 are somewhat unusual in displaying almost perfect sphericity of the residual grains. Figures 29, 31, 32, and 34 are of special interest because they exhibit what is believed to be platelets of either C_4AH_{13}, calcium monosulfate, or C_2AH_8 growing edge-to-face (61) on the interior of the outer or residual shell. The EDXA analysis of Figure 31 is suggestive of C_2AH_8 crystals, since the C/A ratio is low, 2.08. However since the underlying glass has occasionally shown a high aluminum content and since only a few occurrences of this type of morphological feature were available for analysis, the true composition of these hexagonal crystals remains open to question. More common hydration shell and residual grain phenomena are exhibited in Figures 35-36 and 40-50. Figures 37, 38, and 39 represent exceptional grains, in that these grains seem to have been hydrating with their unhydrated portion in close proximity to their hydrated shells, i.e. there is no separation developed between the shell and the residual grain. This brings to mind the inner and outer hydration products noted by Williamson (60) in his studies of C_3S and other pastes.

Rather than present an extensive narrative of these figures, the writer suggests that the reader closely examine these peculiarly hydrating cement grains both for their morphology and for their composition. It should be noted that typically the EDXA analysis shows a C/S ratio of about 3.0 for the residual grain and a C/S ratio from around 2.5 to 2.7 for the residual shell. This implies that these residual grains are probably alite. A discussion of the rate of occurrence of these residual shell, void space, residual grain morphologies is included in the following section, 2.2.2.

For comparison, X-ray diffraction studies were also conducted on the bulk paste specimens. Typically ettringite, calcium aluminate, monosulfate hydrate, alite, belite, and $Ca(OH)_2$ were detected. A typical X-ray diffraction pattern of a paste having little duplex film retained on its surface (in air) is presented in Figure 51. It should be noted that the peak height ratios of the 001 and 101 peaks of $Ca(OH)_2$ approach that recognized for a randomly oriented powder (57). This was the case in other X-ray diffraction (XRD) patterns not presented herein. A discussion of the significance of this result is included in section 2.3.

2.2.2 Three-Day Specimens

Since the first author to recognize the occurrence at the paste-aggregate interface of hydrating cement grains with a residual shell, void space, residual grain morphology was Hadley (20), henceforth in this work, hydrated cement grains showing this peculiar morphology will be termed "Hadley grains." In order to provide an estimate of the distribution of these Hadley grains, photo-mosaics were constructed from overlapping scanning electron micrographs of specimens of all of the cement pastes, hydrated at a 0.5 w/c ratio, and cured for 3 days. These mosaics, compiled from views of the paste side of the paste-glass interface of Type I specimens are presented in Figures 52-55. The exposed interfacial surface areas (i.e. without attached duplex film) measured 23,944--26,421--32,950--and, 26,938 square micrometers respectively. Three-day-old Type I specimens made from cements A, B, C, and D exhibited 22, 29, 30, and 50 clearly exposed Hadley grains respectively. Thus from these

mosaics the respective distribution of Hadley grains was 0.92, 1.10, 0.91, and 1.86 for each 1,000 square micrometers of interfacial surface. While these figures would appear to be insignificant at first glance, on close examination it can be seen that almost all of the grains that are fractured are either empty or contain residual grains; those that are fractured and exhibit morphologies of the type exhibited in Figures 37, 38, and 39 are much more rare. Whether the remaining unfractured grains would exhibit Hadley grain morphology on fracturing is of course impossible to determine, but it is supposed that many of these would. In any event, the phenomenon is worthy of note both from a fracture mechanics point of view and from the standpoint of cement hydration mechanisms.

Figures 56-77 illustrate aspects of the morphology of the paste-aggregate interface, as seen from the glass side, as it evolves during continued hydration. A comparison of the material removed with the glass for one-day-old pastes with that for three day specimens shows that significantly more of the duplex film has separated from the glass at three days. Close observation of Figures 56, 57, and 58 reveals details of the nature of the aggregations of cement grains remaining with the glass substrate at three days. (Aggregations are also present on the one day substrates). There appears to be a continuous phase which has engulfed or retained many of the cement grains. The results of EDXA analysis in Figure 58 implies that it is $Ca(OH)_2$. Figures 59-61 aid in the identification of the continuous, crystalline-appearing material as $Ca(OH)_2$, both from its morphology and its composition. Both Figures 61 and 62 illustrate how the aggregations of cement grains and the continuous lime crystals are held to the duplex film. It is apparent from Figure 62 that not all of the $Ca(OH)_2$ crystals which were in contact with the duplex film have remained with the glass substrate. The dark elongated areas free of cement hydration products apparently represent the traces of $Ca(OH)_2$ crystals. These crystals were formerly in contact with the duplex film on top of the glass and have been removed with the paste.

Examination of Figures 63 and 64 (for specimens prepared with cement A) indicates that by three days the C-S-H gel of the duplex film is beginning to alter its morphology from its original rod-like structure to a "reticulated network" structure as described by Diamond (52). Similar but not quite identical alterations appear to be taking place in companion specimens of pastes of the other cements as evidence in Figures 67, 74, and 77. EDXA analysis presented in Figure 65 for a folded-over area of duplex film adds additional support to the conclusion that the portion of the duplex film in contact with the substrate is composed essentially of $Ca(OH)_2$.

A close-up view of the field shown in Figure 66, Figure 67, reveals the presence of a previously unrecognized structure. The material in the lower left portion of Figure 67 is thought to be a variant form of C-S-H gel, of foreshortened character. Enlargements of the two structures shown in Figure 67 are presented in Figures 68 and 69. The EDXA analysis implies that the two structures are of similar composition, even though both EDXA analyses are perturbed by excess Si from the underlying glass slide. Morphological features similar to these have been noted in the other cement pastes, although photographs are not presented.

Detailed analysis of the portland-blast furnace slag cement paste deposits in Figures 70-74 suggest that the layer of interfacial $Ca(OH)_2$ may not be as extensive for specimens prepared from this cement as for the others. Particular reference to the upper right portions of Figure 71 and Figure 73 suggests that the $Ca(OH)_2$ film may be discontinuous or at least very thin in some regions.

The astute observer may have noticed the occurrence of a new interfacial component in isolated portions of the photo-mosaics presented in Figures 52 and 53. This material appears to exist as a layer between the duplex film and the bulk of the pastes. It is relatively thick and almost appears massive at low magnifications, but at high magnifications, as in Figure 83, is shown to be a porous body composed of smaller units that resemble thin platelets stacked together. This component is

indicated, at low magnification, in Figure 78. Additional views of this material are presented in Figures 79-82 and 85. Typically the material shows a higher C/S ratio than does the flat lying duplex $Ca(OH)_2$ with little elemental substitution. One is therefore led to believe from the location of this new component and from the foreshortened C-S-H gel (Figure 67), that a secondary $Ca(OH)_2$ layer has been deposited between the original duplex film and the overlying cement paste. The appearance of this secondary $Ca(OH)_2$ layer constitutes a major morphological difference between the one-day specimens and the three-day specimens.

As already noted Hadley grains continue to be observed (see Figures 72, 79, 84, 86, and 87). It appears from these figures and Figures 28-50 referred to in section 2.2.1 that Hadley grains may be characterized as follows.

1. The residual or outer shell is typically 1.0 to 1.5 micrometers thick. Chemically the shell exhibits an apparent C/S ratio of about 2.5, indicating that it is probably C-S-H gel.
2. The interior of the residual shell is covered with hexagonal crystals, typically 0.5 micrometer across and 0.1 micrometers thick, whose c-axis is oriented roughly parallel to the shell. The morphology of these crystals, growing edge to face, implies that they are AFm-type products in the classification of Taylor (61).
3. Often the hexagonal crystals serve as buttresses connecting the interior residual grain to the residual shell.
4. The residual grains exhibit apparent C/S ratios around 3.0, implying that they are alite. A significant number of the residual grains appear smooth and sub-angular; a few seem to be etched or at least roughened.
5. The frequency of occurrence of these grains appears small on a total area basis, but only a small proportion of the grains observed at the interface are broken. Most of the fractured grains are of this type.

2.2.3 Seven to Twenty-Eight Day Specimens

The seven, fourteen, and twenty-eight day specimens are examined in Figures 88-145. The manner of presentation is changed in this section as compared to sections 2.2.1 and 2.2.2. Subsection 2.2.3.1 discusses the developing morphology against the 7, 14, and 28-day old glass substrates while subsection 2.2.3.2 deals with the companion paste portions of the specimens. Each subsection continues the established order of presentation with respect to cements used, viz., A, B, C, D.

2.2.3.1 Morphology of the Material Removed with the Glass Substrates

Figures 88-118 include the details of the structural development of material removed with the glass substrates. As can be noted from Figures 88, 97, 104, and 114 very little duplex film remains with the glass after seven days hydration, the areas being mostly black, i.e. clean glass surfaces. Separation appears to have taken place mostly at or very close to the original paste-glass interface. Specimens hydrated for fourteen and twenty-eight days show that this trend continues, leaving less and less material in contact with the glass (see Figures 90, 93, 95, 101, 102, 108, and 116). Exceptions to this trend are shown for cements C and D at twenty-eight days in Figures 111 and 117 respectively.

The material remaining deposited on the glass at seven and fourteen days generally consisted of the duplex film with a few grains of cement attached thereto. For the "A" cement, the C-S-H gel of the duplex film has completed the transformation from the rod-like form to the reticular network structure as shown in Figures 89 and 92. This transition has not been completed in the remaining cements, at least by seven days. In fact, Figures 98, 99, 100, 106, 107, and 115 indicate that for seven-day-old specimens the rod-like structure has been more or less retained for cements B, C, and D. This presents somewhat of a discrepancy between the three-day specimens and these later specimens, since the transition appeared to be proceeding earlier. Unfortunately only small patches of material are available at seven days for comparison. Hence, a clear resolution of this point is not possible. It may be that the C-S-H

transition has proceeded irregularly in some areas, while other areas have failed to transform.

Continued observation of the glass substrate specimens at later ages shows that separation has not occurred at quite the original paste-glass interface. All the cements produce a vaguely mottled appearance on the substrates at low magnifications at either fourteen or twenty-eight days as shown in Figures 95, 101, 102, and 116. At higher magnification these mottled zones are revealed as small "dimples," roughly 0.1 micrometer across, as shown in Figures 94, 96, 103, 109, 110, 113, and 118. These dimples are believed to be small particles of the $Ca(OH)_2$ composing the base of the duplex film, and retained with the glass. The structure left by cement C exhibits what appears to be an etch pattern, different from the others. (See Figures 109 and 110).

2.2.3.2 Morphology of the Cement Paste

As would be expected, the pastes virtually mirror the features detected on the glass substrates. The seven-day specimens, Figures 119, 121, 129, 132, 135, 136, 141, and 143, present a few "windows" (i.e., areas where the duplex film has remained with the glass) permitting the hydration process in the underlying paste to be monitored. Several of these "windows" are enlarged in Figures 120, 128, 130, 131, 137, and 142. Analysis of the underlying components shows that the course of interfacial zone hydration has not changed substantially from that shown for the one and three-day specimens. A few Hadley grains are visible. However the C-S-H transition problem still may not be resolved. Figures 127 and 128 clearly show that the C-S-H on several cement grains exhibit a reticulated structure. Nevertheless it appears that at least the C cement paste has not undergone this transformation by seven days, (see Figure 137). As in the preceding section, no hard and fast conclusion can be drawn since only small portions of the paste structure are available for analysis.

By far the most striking feature of these specimens is the mottled or blotch nature of the interface from the paste side. The first notice

of this discoloration was made with specimen A5007P shown in Figure 121. On casual analysis, this photomicrograph does not appear important. But when the SEM cathode ray tube is switched to maximum contrast, as in Figure 122, the specimen appearance is substantially altered. Not only do both dark and light areas stand out but many elongated crystals are detected just under the duplex film. Frequently the light colored zones exhibit C/S ratios in excess of 25 while the dark areas have C/S ratios equal to or less than 10. In most cases the areas under which elongated crystals are seen exhibit modest C/S ratios (usually around 10) and lower C/A and C/S ratios than do the other light zones. Figures 126, 132, 136, 139, 140, 143, 144, and 145 present a cross-section of the results with all four cements. Steremicrographs, Figures 123 and 124, indicate that the blotchy surface is almost flat. At most, it can be said that the topography of this interfacial surface is gently undulating. The total variation in elevation from dark to light regions is always apparently less than 0.25 micrometers.

The presence of the light and dark zones may be explained as follows:

1. As hydration proceeds past three days the secondary lime layer continues to develop between the duplex film and the bulk of the paste.
2. This layer encapsulates portions of both the duplex film C-S-H gel and the adjacent cement paste.
3. The lighter zones show a high C/S ratio as compared to the dark zones. As previously demonstrated, the secondary $Ca(OH)_2$ yields a high C/S ratio as compared to the $Ca(OH)_2$ of the duplex film. Therefore, EDXA analyses of light colored zones showing high C/S ratios indicate the presence of secondary $Ca(OH)_2$ above the duplex film in the lighter zones, and the darker, low C/S ratio zones are regions in which secondary $Ca(OH)_2$ has not been deposited. Additionally it is known that light zones are regions of high electron emission, which may be associated with the amount of material

present. This would tend to support the supposition that the darker areas are underlain by porous zones. As an alternative explanation, it could be hypothesized that the dark, low C/S ratio areas have thin layers of glass adhering to them. However, it is quite doubtful that glass layers as thin as 0.25 micrometers could influence the EDXA analysis enough to cause substantial reduction in the C/S ratios.

2.3 Summary and Discussion

2.3.1 Summary of the Morphological Development at the Interface

By making use of the early hydration results of Hadley (20) and of the results of this investigation, a general description of the morphological development of the paste-glass interface may be established as follows:

1. Immediately after the cement paste is cast against the glass slide, the cement grains form a loose floc above the substrate as schematically shown in Figure 146.
2. The grains never actually come in contact with the substrate, as visualized in Figure 147; rather they are separated from it either by a layer of water or more likely by an already developing $Ca(OH)_2$—C-S-H gel film precipitated on the clean substrate.
3. Figure 148 depicts that by one day the duplex film consisting of a lower layer of oriented $Ca(OH)_2$ overgrown or intergrown with C-S-H gel has completely developed.
4. At a lower magnification, Figure 149 diagrams the fact that large platelets of substituted $Ca(OH)_2$ have begun to develop and to surround or to encapsulate grains of hydrating cement. On the average, these large hexagonal crystals have a C/S ratio of approximately 10. Judging by the hexagonal sides exposed at the interface, these crystals probably extend from 80 to 150 micrometers into the paste. Although the

crystals shown here are nearly c-axis parallel to the substrate, it is thought that these crystals may vary substantially in their orientation. Perhaps variations in the c-axis orientation may be as much as 60 degrees about the horizontal.

5. Continued hydration results in cross-sections resembling Figure 150. Here it can be seen that the secondary porous $Ca(OH)_2$ layer has begun to develop and join the duplex film to the overlying cement paste. Additionally the cement grains have continued to hydrate producing Hadley grains.

A close investigation of the development of Hadley grains results in the following chronology:

1. As soon as the cement is gaged with water, small plate-like roughly hexagonal crystals begin to form on the surface of the cement grains as schematically illustrated in Figure 151. Subsequently C-S-H gel also begins to grow on this surface.
2. By one day, as schematically illustrated in Figure 152 and 153, an approximately one micrometer thick C-S-H layer has surrounded the cement grain and encapsulated many of the original plate-like crystals. A void space has begun to appear separating the outer residual shell from the inner, hydrating residual cement grain. The residual grain is supported by a few of the original plate-like crystals which have continued to grow.
3. By three days the residual cement grain has continued to hydrate and thereby is diminished in size as depicted in Figure 154. The buttressing crystals have continued to grow. Otherwise no deposition has taken place inside the residual shell. As hydration continues the residual grain will totally disappear and only a hollow shell will remain.

2.3.2 Separation of Paste and Substrate

At one day all cement-glass specimens separated primarily through the void space existing between the duplex film and the overlying paste. A few large aggregations of cement grains remained with the glass as a result of encapsulation by large $Ca(OH)_2$ crystals strongly tied to the duplex film. A few individual grains sometimes also remain with the duplex film.

Three-day specimens exhibited a larger area within which separation between the $Ca(OH)_2$ of the duplex film and the substrate occurred. Additional separation occurred through the void space between the duplex film and the paste, through the contact zone of the duplex C-S-H and the developing secondary $Ca(OH)_2$ layer, and around large cement grain aggregations encapsulated by $Ca(OH)_2$ crystals.

By seven days the duplex film was tied strongly to the paste by both the encapsulating $Ca(OH)_2$ crystals and the secondary $Ca(OH)_2$ layer. A few areas separated through the void space between the duplex film and the paste where secondary $Ca(OH)_2$ was not present. Separation had occurred predominantly along a flat to gently undulating surface at the original interface. It is thought that this fracture surface included both portions of the glass substrate and portions of the duplex $Ca(OH)_2$ film adjacent to the glass.

It is of special interest to note that no separation between the secondary $Ca(OH)_2$ layer and the paste was observed. It appears that the secondary $Ca(OH)_2$ layer is bound so intimately to the paste that separation between it and the paste does not occur.

CHAPTER III - EXAMINATION OF BULK "CONTROL" PASTES

3.1 Specimen Inspection

Type II specimens, i.e. those derived from bulk cement paste, served as a basis of comparison for both the Type I interfacial specimens described in the preceding chapter, and the Type III mortar specimens to be described in Chapter IV. Two methods of specimen preparation were evaluated. Initially it was proposed to saw the dry Type II specimens in two near mid-height. The freshly exposed surface was then to be either ground flat against dry, medium sand paper, or else successively polished flat using #240, #320, and #600 silicon carbide laps with cyclohexane as the liquid medium. It was found that both of these procedures produced unusual surface morphologies. Figures 155-164 are SEM micrographs of polished surfaces for specimens hydrated for various periods. Note that the specimen code is the same as described in Figure 4 with a "C" meaning "control" substituted for the "G" and "P" designations. Figure 155 is a low magnification view showing a mottled appearance, the mottles depicting variations between planar and subsided areas. Closer examination in the stereomicrograph of Figure 156 shows the flat, dark areas to be higher topographically than the lighter, subsided zones. Figure 157 is interpreted as a view of an air bubble which has filled with hydration products abraded from the specimen in the course of polishing. Additional evaluation derived from Figures 158-164 shows that the hydration products bear little resemblance to either the hydration products observed in Chapter II or to hydration products reported by other investigators (52, 53, 54, 60). Based on the EDXA analysis in Figures 156, 164, and 165 the flat dark areas are thought to be $Ca(OH)_2$ and possibly C-S-H which have been smeared and reoriented in an anomalous pattern as a result of the polishing procedure. The seemingly loose angular particles distributed in the topographically lower, light colored, zones are considered to be both hydrated and unhydrated cement particles which have been severely abraded.

After reviewing the results of these polishing procedures, it was decided to investigate the use of fractured specimens. Figure 166, a photo-mosaic, and individual micrographs, Figures 168, 188, 192, and 196, may be used for comparing the morphology of the fractured surfaces with those of the polished surfaces presented previously. Here the letter "F", meaning fractured, is substituted for the "G" and "P" designations described in Figure 4. Obviously, from this comparison the polished surfaces do not accurately reflect the true microstructure of the cement pastes. Therefore, the use of polished specimens was discontinued. From this point forward, reference to the "control specimens" will indicate fractured specimens unless noted otherwise.

3.2 Comparison with Bulk Paste Morphology Observed by Others

Extensive publications dealing with the SEM-observed microstructure of portland cement paste and the minerals which compose it have been presented by Diamond (52, 53, 54), Williamson (60), Chatterji (16, 17, 55, 56), and Mills (62, 63). Mills' results do not seem to be applicable in this comparison because his information was acquired from compressed pastes and from pastes mixed with several admixtures. However, it should be noted that no structures resembling the "calcium silicate hydrate flowers" he describes have been observed in any of the specimens prepared during the course of this investigation.

The present results are similar to those of Diamond, Williamson, and Chatterji. Most of the features mentioned by these authors are exhibited in the photo-mosaic presented in Figure 166. Specifically what appear to be dendritic and reticulated C-S-H structures at low magnification may be observed in Figures 179, 183, 191, and 194 and Figures 175 and 187 respectively. Encapsulation by lime of the cement grains and their hydration products may be observed in Figures 175, 180, 182, 186, and 195. In addition a very few fractured cement grains exhibiting what Williamson described as "inner and outer product" (hereafter termed "Williamson grains") are presented in Figures 176, 181, and 191. These three figures include all of the clear Williamson grains encountered in the study of the bulk or control pastes.

At this juncture, a statement similar to that made in section 2.2.2 concerning the frequency of occurrence of Hadley grains at the interface may be made with reference to the frequency of occurrence of Hadley grains in the present bulk paste specimens. Most fractured grains are either empty or contain Hadley grains, i.e. residual grains with space between the residual grain and the residual shell surrounding it. Those fractured grains exhibiting morphologies analogous to Figures 176, 181, and 191 (i.e. "Williamson grains") are rare. Of course, it is impossible to determine whether the unfractured cement grains conceal Hadley grains or Williamson grains.

A review of Williamson's report, "Solidification of Portland Cement," (60) prompts the following comments. Figures 3.11 (a) and (b) of that report show several β-C_2S grains that my exhibit either hollow shells or Hadley grains on further analysis. In particular the hydrated grain in the center of Figure 3.11 (b) bears a striking resemblance to Figure 169 of this thesis. Additionally Williamson's Figure 3.25 (a) suggests that several possible Hadley grains may have been overlooked. Furthermore, Diamond (64) recently reviewed some of his old photomicrographs and determined that there was indeed cause to believe that hydration structures of the Hadley grain type had been previously overlooked. One particular micrograph of interest is shown as Figure 202. In addition a review of reference (53) shows several examples of what might be empty Hadley grains. Hence it appears that Hadley grains occur more or less extensively even in bulk cement pastes, but have previously been overlooked.

3.3 Bulk vs. Interfacial Morphology

It is apparent after having compared the bulk paste and interfacial microstructure that hydration proceeds in a roughly similar manner in both cases. However there are at least three differences worthy of note:

1. The bulk paste contains less void space than the paste near the glass substrates. A comparison of the photomosaics shown in Figures 166 and 167, both taken at the same magnification, illustrates this difference.

2. A continuous, preferentially oriented duplex film composed of $Ca(OH)_2$ and C-S-H gel is deposited on the substrate and not in the bulk.
3. A porous secondary layer of $Ca(OH)_2$ having no direct counterpart in the bulk, precipitates in some of the void space between the duplex film and the paste at the interface.

As shown earlier with Figure 17, some differences are not readily detectable with the SEM-EDXA combination. X-ray diffraction is sometimes useful in producing supplementary information. In an attempt to utilize this technique the origianl "control" bulk paste specimens were polished flat in order to obtain XRD patterns for comparison with the XRD patterns derived from the interfacial paste specimens. The primary thrust of this work was to investigate Hadley's (20) proposition that the residual or outer shells formed within 200 micrometers of the interface were composed of $Ca(OH)_2$ crystallites oriented c-axis perpendicular to the substrate. When the current XRD investigation was begun it was not known that these shells typically exhibited C/S ratios of approximately three and therefore should be classified as C-S-H gel rather than $Ca(OH)_2$. The XRD analyses were carried out nevertheless, and yielded the results reported in Table 5. The results for the "P" (paste side of the interfacial zone) specimens implied that $Ca(OH)_2$ was preferentially oriented c-axis perpendicular to the substrate. A comparison with the polished control (bulk paste) specimens seemed to imply that for these, either the polishing technique was causing some alteration in structure or that the $Ca(OH)_2$ was oriented c-axis parallel to the long axis of the specimens. As a result of this XRD examination it was concluded that:

1. The $Ca(OH)_2$ on the newly polished surface of the control specimens had indeed been oriented by the polishing action. This conclusion was substantiated both by the SEM investigation discussed in section 3.1 and by Copeland and Bragg's (65) report concerning the preparation of specimens containing $Ca(OH)_2$ for XRD.

TABLE 5

Comparison of $Ca(OH)_2$ Intensity Ratios[1]

Specimen	Intensity Ratio, I_{001}/I_{101}
A6501C	1.59
A6503C	1.58
B6503C	1.40
C6503C	2.00
D6503C	1.13
A6501P	0.83
A6503P	0.82
B6501P	0.95
B6503P	1.46
C6501P	0.63
C6503P	2.53
D6501P	1.06
D6503P	1.25

[1]Intensity ratios are based on the peak heights of the 001 peak and the 101 peak.

2. The data do not confirm that $Ca(OH)_2$ present in the paste up to approximately 200 micrometers into the paste is preferentially oriented relative to the substrate as earlier suggested (20). This point is substantiated from the XRD patterns similar to Figure 51. These diffraction patterns were made using the paste side of the Type I specimens. Typically the specimens chosen retained little duplex film clinging to the paste; therefore essentially all of the X-ray signal came from underlying $Ca(OH)_2$ within the paste. As shown in Figure 51 the 001 peak to 101 peak ratio approaches that recognized for randomly oriented $Ca(OH)_2$ crystals, 0.74 (57). This suggests that the paste just beneath the duplex film exhibits randomly oriented $Ca(OH)_2$ crystals. It is surmised that Hadley's results were strongly influenced by $Ca(OH)_2$ platelets abraded from the duplex film in the course polishing which remained on the specimen's surface.

3.4 Spherulitic Particles

An additional point not previously discussed concerns the large number of small spherulitic or globular clusters occurring near or on the duplex film (Figures 6, 9, 11, 12, 13, and 14). Diamond (53) first noted these occurring in the bulk and suggested that these might be precipitated grains of C-S-H resulting from what Williamson(66) termed "constitutional supersaturation." However, Hadley asserted that these small particles were merely the result of hydration of very small cement grains. This argument seems more satisfying for two reasons:

1. In cements, while the proportion of fine particles by weight is small, this is not true of the relative number of such particles. For example, a far larger number of cement particles are five micrometers in size or smaller than are larger than five micrometers. The ratio of the number of cement particles smaller than 5 micrometers to larger ones ranges from 27 to 52 based on an analysis of particle size distributions presented by Grindrod (67) (see Table 6).

TABLE 6

Possible Particle Size Distributions for a Typical Portland Cement, Based on Grindrod's (60) Results[1]

(a) Grindrod's Data

Nominal Particle Diameter, μm	Weight % Finer	Weight Retained[2]
56	86.3	13.7
40	77.5	8.8
28	64.8	12.7
20	52.3	12.5
14	41.6	10.7
10	32.9	8.7
7	25.2	7.7
5	19.2	6.0
3.5	14.3	4.9
0	----	14.3

[1]Assumes spherical particles having a specific gravity of 3.15.

[2]Weight of particles larger than the Nominal Particle Diameter on a 100 gram basis.

TABLE 6 (Continued)

(b) Numerical Particle Distribution[3]

Assumed Particle Diameter, μm	Number of Particles x 10^7, N_L	Assumed Particle Diameter, μm	Number of Particles x 10^7, N_S
74	2.05	56	4.72
55	3.21	40	8.30
39	13.00	28	35.10
27	38.50	20	95.00
19	95.00	14	236.00
13	235.00	10	527.00
9	640.00	7	1360.00
6	1690.00	5	2910.00
4	4600.00	3.5	6900.00
3.4	22,100.00	2.0	108,000.00

(c) Relative Proportion of Five Micrometer Diameter Particles on a Number of Particles Basis

Assumed Particle Size Distribution	N_L[4]	N_S[5]
Total No. Particles $>$ 5 μm, L	1,027	2266
Total No. Particles $<$ 5 μm, S	28,390	117,810
S/L	27	52

[3]The range of particle size distribution is considered by assuming either all the particles are only incrementally smaller than the preceding sieve (left column) or are incrementally larger than the sieve on which they are retained (right column).

[4]Number of particles assuming large diameters

[5]Number of particles assuming small diameters

2. A significant number of these grains, which lie on the duplex film, have fractured. Usually they show a smooth interior and give the impression that they were formerly filled, Figure 13, or may even still retain a residual grain (see center of Figure 14). Small particles of this size have been observed in the bulk as well as at the interface. Whether these particles are more abundant in one location as opposed to the other is difficult to discern. However, owing to the loosely compacted nature of the cement flocculated immediately above the substrate, it is likely that many of these small grains fall through onto the duplex film as does sand through coarse aggregate.

Further consideration raises the question of the composition of these particles. Owing to their small size EDXA analysis cannot be of much value since substantial X-ray interference from the surrounding components undoubtedly occurs. However it may be hypothesized that a large percentage of these particles are finely ground gypsum. Supposedly in the grinding process the softer gypsum would tend to abrade much more easily than the harder cement minerals, thereby yielding a disproportionate number of five micrometer size gypsum particles. To examine this hypothesis a Stokes law settlement analysis and an accompanying chemical analysis was executed.

The experimental procedure* consisted of dispersing the cement in a solution composed of ethyl alcohol and $CaCl_2$. The cement was allowed to settle. Specimens of 100 ml were pipetted from the supernatant and from the coarse material at the bottom of the settling cylinder. The results of this analysis are given in Table 7. The results did not indicate that the five micrometer size material was substantially gypsum. There is some indication that the gypsum may indeed crush to a slightly disproportionate fine size. However a typical comparison of SO_4^{-2} contents for cement B yields : 3.62 % in the dry cement, 7.10 % in the supernatant liquid, and 4.63% in the settled material at the bottom of the cylinder.

*See Appendix VI for details of analysis.

TABLE 7

Results of Analysis for SO_4^{-2} in the Minus Five Micrometer Size in Portland Cement[1]

Material	Description	Average % SO_4^{-2} (by weight of cement)
cement A[2]	supernatant[3]	7.77
	settled residue	2.46
cement A	supernatant	7.86
	settled residue	4.51
cement B	supernatant	7.02
	settled residue	4.53
cement clinker	supernatant	0.43
	settled residue	0.42

[1]Appendix VI details the analytical procedure

[2]This sample was prepared with a 3% by volume suspension as compared to 1% for the others.

[3]The supernatant solution contained nominally minus five micrometer material.

3.5 Summary

In summary the following important points should be noted:

1. Polished control paste surfaces exhibit significant artifacts which would contribute to faulty SEM-EDXA and XRD analysis.
2. The bulk paste morphology as exhibited by fracture specimens is different from the interfacial morphology in three principle ways.
    (a) The bulk paste contains less void space than the paste nearest the substrate.
    (b) The porous secondary lime layer formed just above the interfacial duplex film has no counterpart in the bulk paste.
    (c) No structure having the composition and orientation of the duplex film exists in the bulk.
3. Hadley grains are present both at the interface and in the bulk.
4. Small spherulitic particles observed both in the bulk and at the interface are most probably hydrated cement grains.

CHAPTER IV - EXAMINATION OF MORTAR SPECIMENS

4.1 Specimen Preparation

As detailed in Appendix I, a series of mortar specimens (here designated as Type III) were formulated at various w/c ratios with various volume fractions of aggregates. A standard two week curing period was provided for all of these specimens. They were then thoroughly dried, loaded to a prescribed fraction of their ultimate strength and then fractured in preparation for SEM inspection.

There were several reasons for following this preparation sequence. The main reason was the desire to determine the influence of stress level upon interfacial crack initiation and propagation. Drying the specimens before fracturing is helpful in microstructural examination. If specimens are not dried prior to loading and fracture, there is significant evidence (20) that $Ca(OH)_2$ precipitating from the pore solution on drying after fracturing obscure much of the fracture surface microstructure. The fracture surfaces to be inspected were prepared by fracturing the cylinders transversely. There is an obvious question concerning the introduction of additional cracks as a result of this fracturing. Unfortunately, the only alternative preparation technique, i.e. sawing the specimens in two, is subject to even more important problems, viz.:

1. The high probability that sawing introduces many aggregate-paste interfacial cracks. If the mortar system were one containing aggregates equal in hardness to the cement paste and perfectly bonded thereto, no problem would exist. On the other hand one should consider that in the case of silica sand grains in a two-week-old paste, sawing promotes substantial differential strains between the paste matrix (having a Moh's hardness of 3 to 4) and the aggregate (having a Moh's hardness of 7). Thus this type of preparation should necessarily introduce interfacial cracks.

2. Any form of sawing is by nature an abrasive process. It has already been shown that even modest polishing introduces substantial artifacts and alterations onto the surface being prepared for analysis.
3. If the sawing were done without a cooling fluid, the interior of the mortars would be subjected to heat generated by friction. On the other hand if a cooling fluid were used, many questions concerning possible solution and reprecipitation of cement compounds would require investigation.

In contrast the fracturing procedure had several advantages:

1. By definition, at least one undisputable load-induced fracture surface would be prepared for observation.
2. The strain field caused by the fracturing, if ideally accomplished, would be at right angles to the existing load-induced cracks. Hence when the specimen is inspected the viewer should be able to distinguish between two crack patterns: one parallel and one normal to his line of sight.

Additional consideration was given to the selection of the type of sand used in the mortar. It was desirable to choose an aggregate that was clean, uniform and closely resembled naturally occurring and conventionally used material. Two available aggregate materials seemed to suit these requirements: (a) a manufactured calcite sand and (b) silica sand meeting the requirements of A.S.T.M. designation C-109. The calcite sand was rejected because there existed the strong likelihood that a substantial amount of fracture would occur through the aggregate, i.e. along its cleavage planes (4, 20). Fracture of this type would obscure the potential interfacial fracture zone of interest. The Ottawa silica sand was then chosen in view of its strength and difficulty of cleavage.

4.2 Surface Morphology of Ottawa Sand Grains

Some knowledge of both the composition and surface microstructure

of the sand seemed necessary before beginning the investigation of the sand-paste interface. Initially a brief literature review concerning "Ottawa sand" was undertaken. Other than the determination that it is a well crystallized product of partially metamorphosed quartzite coming from Ottawa, Illinois, little information was available. There does not seem to have been substantial prior interest in the SEM surface characterization of sand grains. One paper (68) by Lucchi and a short atlas by Krinsely and Doornkamp (69) have been marginally helpful in connection with the surface characterization. However, the only suitable method of gaining the desired information was to proceed with an SEM investigation of the sand itself.

Specimens consisting of Ottawa sand grains selected at random were placed on double stick tape affixed to an aluminum specimen stub. These grains were then coated with carbon and chromium, in the manner that had been used with the cement specimens. No effort was made to clean or otherwise alter the sand grain surfaces. The mounted sand grains appeared as in Figure 203 at low magnification. Here it can be seen that the grains are sub-rounded with a few sharp projections. The EDXA results indicated that the grains contained Ca, Al, and Mn as minor constituents in otherwise pure SiO_2. At a slightly higher magnification, Figure 204, the surface exhibits vast expanses of rough topography. Progressively higher magnification views of this broken topography are presented in Figures 205, 206, and 207. Krinsely and Doornkamp (69) indicated that this type of morphology is the result of diagenesis; more specifically, the solution and reprecipitation of silica. In addition to the rough topography, there are regions on the surface, such as that marked by point number 1 in Figure 204, and shown right of center in Figure 208, which appear flat and smooth with parallel surface striations. These may be unweathered crystal faces that have grown in a cavity isolated from the remainder of the grain, or "breakage blocks" and cleavage plates as described by Krinsely(69). Figures 209 and 210 present two additional microstructures noted on the Ottawa sand grains.

The more obvious of these is the large dished-out area in the upper left of Figure 209, similar structures being visible in Figure 204. These features are thought to be areas formerly fractured conchoidally and later subjected to some kind of chemical smoothing (69). The other microstructural feature noted in Figures 209 and 210 are crack patterns that seem to outline polygons on the surface of the sand grain. According to Lucchi (68) such cracks may be attributed to "the shrinkage of an isotropic altered layer of silica," the shrinkage being caused by daily variation in moisture and temperature. Although Lucchi was referring to desert sand grains in his analysis, it is conceivable that the same crack patterns could result from alternate freezing and thawing cycles in temperate climates.

In summary, the surfaces of the Ottawa sand grains exhibited several distinct classes of surface features the details of which should be kept in mind in examining the microstructure of mortars made from that sand. Furthermore, it was established that other elements (Ca, Al, and Mn) are present in addition to the silica.

4.3 Comparison of Microstructures of Sand-Paste Interfaces in Mortars with the Glass-Paste Interfaces

As mentioned above, specimens prepared at several w/c ratios and sand concentrations, C_v, were examined. The combinations investigated are outlined in Table 3. The specimen code used for these specimens is described in Figure 211. At the outset it was recognized that sand volume fractions of 30% ($C_v = 0.30$) most nearly represented the typical composition of mortar in concrete. However specimens made with $C_v = 0.60$ were also examined. Figure 212 clearly shows the high porosity resulting from such high sand concentrations in low w/c ratio, 0.32, mixes. Obviously this porosity resulted from poor consolidation. As a result of this open structure not typical of concrete, both mixes having the high sand concentrations were omitted from this discussion.

Although this subsection deals specifically with microstructural comparisons between Type I and Type III specimens, the reader is

requested to also note the location and size of cracks which appear in the photomicrographs presented.

4.3.1 Mortars of w/c = 0.32, C_v = 0.30

Specimens of low w/c ratio (0.32) and of lower aggregate content (C_v = 0.30) were examined in detail. In these specimens little bleeding occurred. Figure 213, for such a specimen examined at low magnification, shows stereoscopically the transverse fracture surface. Quartz grains were never found to be fractured in these or any other mortars examined. All fracture surfaces followed the outline of the aggregate particles. An indication of how closely the outline of the sand grain was followed may be obtained from Figure 214. In addition to the blocky nature of this sand grain one should note the grey film under points numbered 1, 4, and 5. This is a low magnification view of the duplex film forming on the aggregate. Also note that the separation of paste and aggregate has occurred both just above the duplex film in some areas and between the duplex $Ca(OH)_2$ and the aggregate in others. Figures 215, 216, and 217 are progressive enlargements of a sand grain socket (i.e. where a sand grain was pulled out in fracturing). At the bottom of this socket the familiar blotchy duplex film appears, underlain by several elongated features just as were noted in the seven day and older Type I specimens.

Details of several features of the interfacial zone that developed between another sand grain and the paste are illustrated in a series of micrographs constituting Figures 218-221. Figure 218 shows the elongated socket at low magnification. Figure 219 is a somewhat enlarged view, and shows two distinct zones at the base of the socket, a smooth grey area in the lower portion and a somewhat broken zone in the upper portion. The lower portion is the $Ca(OH)_2$ layer of the duplex film that was initially deposited on the sand grain. The broken upper region reveals useful information on the details of the region on the paste side of the duplex film.

Figure 220 is an enlargement of roughly the central portion of the upper broken zone. Large elongated crystals of $Ca(OH)_2$ oriented

with their c-axis parallel to the interface are visible (spots 1 and 3); a massive $Ca(OH)_2$ crystal extending to roughly the same level (i.e. touching the previously existing duplex film) is also present, spot 2. In Figure 221 is an enlargement of another region in the upper broken zones of Figure 219 to the left and slightly above that shown in Figure 220. Figure 221 shows a region of unbroken duplex film (spot 2, lower left portion). Extending toward the upper right portion of the micrograph is the projection of a large elongated $Ca(OH)_2$ crystal (spot 3) similar to those observed in Figure 220. There is one important additional feature visible on this micrograph; a zone of small $Ca(OH)_2$ platelets locally oriented parallel to each other that constitute the layer of secondary $Ca(OH)_2$ visible at point number 1 and in other regions of the micrograph. This zone has been deposited just under the original duplex film.

An important feature in the 1-000 specimens (w/c = 0.32, subjected to "0" load) is apparent in Figures 222-224. In these unloaded specimens it is seen that cracks exist near the paste-aggregate interface. Typical locations of these cracks are illustrated in Figures 223 and 224. They occur seemingly at the original paste-aggregate boundary. Separation has occurred in these specimens between the aggregate and the base of the duplex film. An equally important feature of these cracks is their width, typically one micrometer.

Closer inspection of the morphology of the duplex film as it occurs in these mortars is afforded in Figures 225-227. The stereomicrograph of Figure 225 clearly shows that the film rises above the sand surface approximately one micrometer. The EDXA analysis in Figure 226 demonstrates that this film is chemically like the duplex film found at the paste-glass interface in Type I specimens, which also showed an apparent C/S ratio of about 0.22. Morphologically, the additional enlargement, Figure 227, shows that the film in the present specimen is like the glass-paste film showing foreshortened C-S-H gel (Figures 66-69).

A stereo view into one of the sand grain sockets is shown in Figure 228. On enlargement in Figures 229 and 230 a smooth dimpled discontinuous layer believed to be the duplex film reflecting its former contact surface contour is shown. Figure 230 leads one to believe that the secondary $Ca(OH)_2$ layer normally found behind the duplex film is absent. Instead what are probably ettringite needles formerly in contact with the duplex film are exhibited. Figures 231-233 are additional views of the duplex film as ordinarily underlain by secondary $Ca(OH)_2$ and what were previously recognized as the edges of hexagonal crystals. Figure 232 exhibits the light zone--dark zone, blotchy, appearance and EDXA results noted on the older Type I "P" specimens. Figure 233 furnishes additional proof of the existence of a secondary $Ca(OH)_2$ layer (spot 1) in mortars.

As noted in Figure 230, the secondary $Ca(OH)_2$ layer may not always be present. Figures 234 and 235 seem to support this. Here again the secondary $Ca(OH)_2$ layer seems to have been replaced by ettringite needles bridging the void between the duplex film clinging to the aggregate and the paste on the left. The presence of the ettringite needles across the crack provides clear evidence that the crack was present prior to loading. In addition to the ettringite needles across the crack there are a few well formed hexagonal plates (partly on edge) clinging to the paste on the aggregate, as indicated in Figures 234 and 235. The presence of these well formed crystals suggest that the interfacial region had considerable void space and was filled with liquid. Crystals of this type were also found occasionally at paste-glass interfaces of Type I specimens. Figure 236 is a close-up view of a region of the back of the duplex film clinging to the aggregate surface, as was shown at lower magnification in Figure 235.

Earlier Scholer (70) and Alexander (71) alluded to the probability of both chemical and mechanical bonding occurring between cement paste and aggregates. Figure 237 seems to show an example of these two types of bond. The features similar to that marked by point number 1 belong

to the sand grain. At the upper right of this micrograph there occurs a portion of duplex film adhering to what may be a smooth portion of the sand grain surface. One might hypothesize that this adhesion is the result of chemical bonding (Van der Waals or diffusion (72) bonds) as there does not appear to be any available mechanism for mechanical interlock between this duplex film and the aggregate surface. In contrast there appear to be some cement hydration products entrenched in a micro-fissure of the sand grain near the center - left portion of the micrograph. It is possible to suppose that the mechanical interlock resulting from the entrenchment of cement products in fissures of this type promotes adherence based on a decrease in the freedom of movement between the paste and aggregate resulting in a bond that is independent of chemical interaction, i.e. a mechanical bond. Based upon this brief examination it is not possible to do more than to continue the hypothesis that both bonding mechanisms operate in paste-aggregate systems. Nevertheless, owing to the rough surface character of aggregate and the possible precipitation of hydration products in the associated surface irregularities the operation of mechanical interlock bonding continues to be a reasonable supposition.

Figures 238 and 239 are from the 1-060 specimens. As shown earlier in Figure 222, cracks continue to propagate at the interface rather than through the bulk paste even at high load. Additionally, portions of residual cement grains seem to be attached to the sand grain surface in these specimens similar to what happened at paste-glass interfaces examined earlier (Figures 6, 9, 11, 12, 13, and 14).

Examination of the 1-100 specimens (w/c = 0.32, subjected to failure loads) has shown no morphological differences from the other low w/c ratio mortar specimens. Some change in the crack propagation sequence may have occurred, as will be discussed in section 4.4.

4.3.2 Mortars of w/c = 0.50, C_v = 0.30

The sand grain in Figure 240 for a specimen prepared at a high w/c ratio, exhibits much the same surface characteristics as that shown in

Figure 213 for the low w/c ratio mortar. There are dark areas representing the removal of duplex film and grey zones indicating its presence. As in the 0.32 w/c ratio material, the duplex film is obvious at higher magnification, Figure 241. Here both the foreshortened and the reticular C-S-H gel component are obvious. Figure 242, would be identical to what would be seen on micrographs of the glass side of paste-glass interfaces (Type I "G" specimens), and could easily be confused with that kind of specimen, were it not for the labelling indicating it to be a mortar. This photomicrograph exhibits not only the characteristic reticular C-S-H gel but also includes small adhering cement grains (1-5 micrometers in diameter) and on-edge platelets.

Heretofore the occurrence of large aggregations of cement grains has not been mentioned for mortars as they are not common in comparison with their frequency of occurrence at glass interfaces. However Figure 243 depicts a large aggregation of such cement grains engulfed by what are probably substituted $Ca(OH)_2$ crystals.

Figures 244-246 depict the occurrence of massive probably highly substituted $Ca(OH)_2$ crystals just behind the duplex film. Hadley (20) suggested that this type of structure provided primary adhesion between the duplex film and the paste. However, in the present mortar specimens it has not been recognized as a general phenomenon, although it does occur at the boundaries of some sand grains.

Progressive enlargements from Figures 247-250 show the arrangement and composition of the secondary lime, $Ca(OH)_2$ crystals, and other hydration products just behind the duplex film. A comparison of these figures with Figures 219-221 and 229-234 illustrates the direct relationship between w/c ratio and the porosity on the paste side of the interface. Figures 251 and 252 furnish a first glimpse of Hadley grains occurring near the paste-aggregate interface in mortar. Characteristically those few Hadley grains detected were devoid of their residual cement grains. Perhaps this is an indication of their complete hydration in the two-week curing period allowed. It should be recalled that near

the paste-glass interface studied earlier, residual shells could not be observed after about three days of hydration because of the overlying duplex film.

Another stereomicrograph of the fracture surface is presented in Figure 253. Figures 254-262 serve as additional views of microstructural components already described but in this case on a 3-030 specimen. Figure 255 is particularly deserving of note as it depicts the duplex film with both $Ca(OH)_2$ and (in this case) sheaf-like C-S-H components.

Figures 263 and 264 further illustrate the morphology of cement grain aggregations adhering to the aggregate. Here it can be seen that even in mortars the engulfing $Ca(OH)_2$ crystals continue to orient themselves roughly edge-on to the substrate. Additional recognition of the presence of Hadley grains is shown in Figures 265-267. Figures 268 and 269 from 3-100 specimens show the presence of an interfacial crack which has propagated between massive lime crystals and the duplex film on an aggregate. In Figure 269 it is clear that separation has not been between the duplex film $Ca(OH)_2$ and the aggregate. This would seem to imply that the massive $Ca(OH)_2$ crystals do not promote strong interfacial bond.

4.4 Crack Initiation and Propagation

In all the mortar specimens examined, cracks were observed to exist near the original paste-aggregate interface. Generally the cracks occurred at the cement paste--duplex film boundary or between the $Ca(OH)_2$ of the duplex film and the aggregate. Cracks following the general outline of the aggregate were not observed to occur more than thirty micrometers from the aggregate.

The most surprising observation was that cracks surrounding the aggregate particles were found to be present in specimens representing all the stress levels examined; 0%, 30%, 60%, and 100% of the ultimate strength. Indeed the cracks occurring in the loaded specimens are not surprising. However those appearing in the 1-000 and 3-000 (non-loaded) series were disconcerting at first. Some evidence of these cracks were

noted in the foregoing figures. However, the presence and location of the interfacial cracks is best depicted by photo-mosaics rather than by individual micrographs.

Figures 270 and 271 are photo-mosaics of the 0.50 w/c ratio mortar specimens which have been subjected to 0% and 60% respectively of their ultimate strength. A close examination around the left side of the sand grain in Figure 270 reveals an approximately one micrometer wide crack following the duplex film-paste boundary. Figure 271 shows a similar size crack following within a 30 micrometer distance of the sand grain for the 3-060 specimen. Even this crack comes very close to the original interface in several places.

A much clearer insight into the true crack location can be obtained from Figure 272 for a non-loaded mortar specimen and Figure 273 for a specimen loaded to 60% of its ultimate strength. Both these mosaics are from the more dense 0.32 w/c ratio pastes. A distinct advantage of viewing these specimens is the readiness with which the crack may be followed; there was little difficulty in distinguishing between paste porosity and cracks as there occasionally was with the higher w/c ratio material. Using both these figures it is apparent that the crack existed prior to loading, and as higher loads developed the crack propagated near the aggregate interface out into the bulk paste.

It is hoped that by this point the reader has raised some questions concerning the origin of the 0% stress level cracks. A simple (but perhaps erroneous) answer would be that these cracks were both initiated and propagated by the transverse fracture process. It has already been reasoned that this should not occur for ideal transverse fracturing. The alternative mechanism involves shrinkage caused cracking. To investigate the suitability of this mechanism as an explanation several 0.32 and 0.50 w/c ratio mortars with C_v equal to 0.30 were cast against glass substrates. Presumably such specimens would:

1. simulate the contact between coarse aggregate and mortar; and

2. allow the inspection of fine aggregate-paste interfaces in specimens which had never been loaded or fractured, but which would likely have undergone drying shrinkage.

After examining the mortar-glass interfaces it was determined that virtually the same microstructure developed as had been noted with the Type I and III specimens. One exception occurred near the contact between sand grains and the glass substrate. Figures 274 and 275 show a sand grain which was near the glass substrate. The sand grain appears to have been stripped of some duplex film. The presence of this component indicates that the two "aggregates," sand and glass, were not in true contact but instead were separated by their respective duplex films. The two films perhaps became intergrown or were tied together by some other hydration products (e.g. secondary $Ca(OH)_2$).

Figure 274 and the photo-mosaic of Figure 276 clearly show that cracks do occur near the paste-aggregate interface even in specimens which have never been loaded. As in all the Type I specimens, physical separation between glass and paste occurred spontaneously on drying. Furthermore both the presence of boundary cracks and of obviously stripped away duplex film indicate that cracks exist near the aggregate interface prior to any loading. This can be proved from this work only for specimens which have been thoroughly dried before exposure to the SEM and obviously suffered significant shrinkage strains. However, it would seem likely that at least some cracks of this type exist in concretes which have been subjected to either modest drying in the atmosphere or cycles of drying and wetting.

Previously, it was noted that interfacial cracks observed in the 3-100 and 1-100 specimens did not appear to differ from those occurring in the specimens subjected to lower stress. However, the mode of crack propagation does appear to have changed. Figure 277 is a low magnification view of one of the few exceedingly large cracks generated at failure. Cracks of this type are not only grossly larger than the paste-aggregate cracks, but also propagate randomly through the mortar. They do not follow the paste-aggregate interfaces. Since there are only a few such

cracks in any one failed specimen, their random path nature is believed to be related to dynamic load conditions generated in the conventional compression tests. With the advent of dynamic loading, cracks no longer propagate in a stable manner. Instead of following the lowest strain-energy paths (i.e. the weak zones near paste-aggregate interfaces) those few cracks subjected to the highest strain conditions seek to release this energy as rapidly as possible rather than to follow the paths of least resistance. Additional discussion of this phenomenon follows in section 4.5.

4.5 Comparison of Observed Crack Patterns with Results of Previous Research

Prior to discussing the results of previous research, it will be instructive to consider the X-ray and optical techniques previously used for concrete microstructure evaluation. Even in the most recently reported work (73), 1974, little attempt was made to improve upon the X-ray and optical techniques earlier used by Hsu (10). The X-ray techniques are all similar in that they function by passing X-ray through a thin slab of concrete which then impinges on a photographic plate. Since cracks represent regions of low X-ray absorption, their locations are marked by zones of higher X-ray intensity and a trace of the crack pattern is visible on the photographic plate. Of the papers reviewed (7, 10, 11, 73), using this technique, only one made any attempt to evaluate its resolving power. Robinson (11) using 2.75 inch thick concrete slices, estimated the resolving ability of the technique at approximately 0.3 millimeters, i.e. 300 micrometers. There is some reason (74) to believe that thinner specimens might improve the resolving capability of this technique, and indeed slices only 0.15 inches in thickness were the principle specimens used by Slate and Olsefski (7). Nevertheless, these authors did not report any efforts to optimize their procedure for increased resolution. After reviewing the single X-ray picture included in Hsu's (10) study it does not seem that a resolving capability significantly greater than that reported by Robinson (11) was attained.

Other methods of studying crack behavior involve optical techniques. All optical magnification techniques applied to this problem have

utilized between 30X and 50X magnification. If one considers that the human eye's resolving limit is approximately 0.2 micrometers (75), then the smallest resolvable morphological feature at such magnification would be approximately 4 micrometers. The stable cracks observed in this work are about 1 micrometer across.

Even without considering the complications of artifacts introduced by polishing and of depth of field, it should be obvious that previous researchers have been privy to only a small portion of the morphology associated with the fracture process. Hence, it should not be surprising that cracks in the concrete mortar phase have not been observed until 70-95% of the ultimate load (10). That is to say that these cracks were not noted until the specimen had deformed to the extent that the mortar cracks had begun substantial lengthening and widening.

Many authors (10, 11, 12, 23, 76, 77, 78, 79, 80) have known or suspected for some time that the shape of the stress-strain curve is associated with internal microcracking. Supposedly this microcracking may begin at stresses as low as 25-30% of the ultimate strength of the concrete (78).

Hsu (8) has summarized the crack-load relationship as follows:

1. "Microcracks can be divided into two types--bond cracks between aggregate and paste-mortar, and cracks through the paste-mortar (called paste cracks for convenience).
2. Bond cracks exist even before the concrete is subjected to any load, while paste cracks are negligible at that stage.
3. Bond cracks increase (both in length and in width) with increasing strain in both the ascending and the descending branch of the stress-strain curve.
4. In general, bond cracks first occur around the large aggregates.
5. Paste cracks begin to increase noticeably at strains of 0.0012 to 0.0018, or in terms of load, at about 70-95% of the ultimate load.

6. Paste cracks bridge between the nearby bond cracks and usually form where distances between coarse aggregates are relatively small, thus providing only a short length of paste to be cracked between bond cracks.
7. Concrete is very extensively cracked in the descending branch of the stress-strain curve. The extent of cracking seems more directly associated with the slope of the stress-strain curve than with the absolute amount of strain."

It should be noted that the following definition of terms was used in Hsu's (8) work:

a. paste cracks - cracks through the paste-mortar phase
b. bond cracks - cracks around the aggregate, and
c. aggregate - coarse aggregate.

The results of the current investigation are not in conflict with Hsu's findings on the scale at which he was able to observe. However the techniques used in this investigation have provided additional information. Bond cracks near coarse aggregate-paste interfaces and fine aggregate-paste interfaces exhibit the same morphology. This is substantiated by a comparison of the results for the Type I specimens (where the glass substrate represents the coarse aggregate) and those for the Type III (mortar) specimens. These bond cracks exist simultaneously near both the coarse and fine aggregate boundaries prior to loading. Additionally, it may be stated that cracks within the mortar phase begin to enlarge or propagate, rather than to initiate, at 70-95% of the ultimate load. Prior to this load range the cracks were probably not observed by Hsu and others because their observation techniques did not furnish sufficient resolution.

Some question has been raised concerning the often observed result that concrete failed in unconfined compression often fractures "through" rather than "around" aggregate particles. Explanations for this phenomena have been given both by Hsu (9) and by McCreath (15).

Hsu observed that:

> "A surprisingly small amount of cracking was observed through aggregate particles, even at high strains just prior to disruptive failure. This was true even though the same concrete showed large amounts of failure through the aggregate when a failed cylinder was observed by eye after conventional testing which gave an "hour-glass" type of failure. Compression loading with restrained ends may force final shear failure through some of the coarse aggregate, after an extensive network of other cracks had been formed prior to the final disruptive failure."

The key phrase for understanding this statement is "conventional testing." In a conventional test not only are the ends of the cylinder restrained both by friction and the capping material but the specimen is unprotected from the strain energy stored in the testing machine. Therefore in a conventional test the concrete is subjected not only to combined states of stress but to a terminal dynamic load as a result of the testing machine releasing its stored energy on a specimen only marginally able to resist. Of the two effects, the latter is probably more influential. Both Hsu (9) and McCreath (15) avoided this dynamic loading problem. Hsu by placing aluminum channels on either side of the compression head thereby providing a continuous restraint against the sudden strain release at specimens failure, and McCreath by placing the specimen in a triaxial state of stress. As a result both authors noted only a few fractures through the aggregate. These few occurrences were usually associated with aggregates having a layered structured or easily cleaved planes. Hence it seems necessary to assume that fracture through the aggregate is an artifact of the loading condition, and may not apply in the general case of concrete fracturing.

4.6 Summary

The microstructure developed at the interface between paste and glass (Type I specimens) and between paste and aggregate grains (Type III

specimens) is the same except that sand grain-paste interfacial regions occasionally do not appear to develop an extensive secondary $Ca(OH)_2$ layer. In these cases the duplex film is backed by either massive $Ca(OH)_2$ crystals or by ettringite needles growing from the paste toward the aggregate. The frequency of occurrence of these last two features is limited; typically the duplex film on aggregates is backed by a layer of secondary $Ca(OH)_2$.

The separation between paste and aggregate was observed to occur predominately at either the duplex film-paste boundary or at the duplex film-aggregate boundary. In all cases observed, the separation occurred within approximately 30 micrometers of the aggregate surface. An occasional cluster of cement grains encapsulated by large $Ca(OH)_2$ crystals was observed to have been pulled out from the paste and remained on the aggregate surface.

The existence of so-called "Hadley grains" at the paste-sand interface was observed in the Type III specimens. However, the frequency of occurrence of these features was not extensive. It is possible that the occurrence of these Hadley grains could have been obscured by deposition of other hydration products near the interface. The existence of this morphological feature does not appear to significantly influence either fracture initiation or propagation in mortars.

The observations made in this study serve to extend the results of earlier work by Shah (12, 81), Robinson (11), McCreath (15), Moavenzadeh (14, 82), and Hsu (9, 10). It has been noted that many microfracture-microstructure features are beyond the resolution of the research tools utilized by these workers. Additionally it appears that the possible presence of microcracks around sand grains within the mortar prior to loading was discounted at the outset of these earlier studies. In the present work the presence of such cracks has been shown to be extensive in specimens dried but not loaded.

CHAPTER V - SUMMARY OF FINDINGS

5.1 Morphological Development of Hydration Products Near the Paste-Aggregate Interface

The research shows that the same microstructure develops at the paste-aggregate interface and the paste-glass interface. Chronologically the structure develops as follows:

5.1.1 Microstructure at One Day

By one day a duplex film composed of a continuous, 0.25 to 0.50 micrometer thick, layer of $Ca(OH)_2$ either overgrown or intergrown with rod-like C-S-H gel has precipitated on the aggregate surface. The total thickness of this film is typically 1.0 micrometer. The $Ca(OH)_2$ precipitates preferentially (but not perfectly) with its c-axis perpendicular to the substrate surface.

Large crystals of substituted $Ca(OH)_2$ are observed to grow and to encapsulate and engulf aggregations of cement grains. Usually these crystals are a minimum of one micrometer thick and about thirty to fifty micrometers on a side. They are observed to grow roughly c-axis parallel to the aggregate interface.

Many of the cement grains at the interface fractured in separating the substrate from the paste. Of these, all that could be observed began to hydrate by a through-solution process. These fractured grains exhibit a residual shell-void space-residual grain structure, termed "Hadley grains." These residual grains usually have a C/S ratio of approximately three. They are often supported by the shell in the form of roughly hexagonal crystals growing edge-on to the residual shell and to the residual grains. These hexagonal crystals are believed to be of the AFm (61) crystal type characteristically. They are quite small at one day since the void space between the shell and the residual grain is typically only one micrometer.

5.1.2 Microstructure at Three Days

After three days the Hadley grains are found to have continued their peculiar hydration pattern. The interior void space has continued to increase. The residual grain has continued to diminish. And the interior hexagonal crystals have continued to grow, thereby bridging the space between the residual shell and the residual grain. Except for this, no additional deposition has occurred within the residual shell. The residual shell retains its original thickness, about one micrometer.

The most notable development by this time is the development of a porous secondary $Ca(OH)_2$ layer having a C/S ratio usually larger than twenty five and an estimated minimum thickness of one micrometer. This layer grows between the duplex film and the cement paste. The secondary $Ca(OH)_2$ is extensively developed, but regions where it is absent are detectable. This $Ca(OH)_2$ layer serves to join the duplex film and paste. Where the secondary $Ca(OH)_2$ layer is absent, massive lime and ettringite are observed to form a porous connection between the paste and duplex film.

5.1.3 Microstructure at Seven Days and Beyond

By seven days the secondary $Ca(OH)_2$ layer had almost completely bound the duplex film and the paste together in the glass-paste interface specimens. However in the mortar specimens this does not seem to have occurred to the same extent. Rather large areas of duplex film were observed remaining on the aggregate after separation. Consequently large areas of secondary lime appeared on the paste adjacent to the aggregate surfaces.

5.2 Crack Initiation and Propagation

In concrete and mortar systems cracks are present near the paste-aggregate interfaces prior to any applied load. These cracks are the result of drying shrinkage induced strains. Some cracks of this nature apparently exist in wet concretes. Evidence for this statement is provided by the observed occurrence of ettringite needles growing across some of these cracks.

The results of this investigation show that paste-aggregate cracks always initiate within thirty to forty micrometers of the aggregate surface, and predominately within two micrometers of the aggregate surface. Most of these cracks occur either between the duplex film $Ca(OH)_2$ and the aggregate surface, or between the duplex film and the overlying cement paste material. Hollow "Hadley grains" do not appear to play a significant role in the interfacial cracking phenomena. No separation between the secondary $Ca(OH)_2$ and the cement paste was ever observed.

The application of an external load causes the largest, properly oriented cracks to begin to propagate. These cracks exist at the interfaces between the paste and the large aggregate particles. As the load is increased, cracks at the interface between the paste and fine aggregate grains also begin to enlarge. A significant time lag may occur before aggregate-interfacial cracks begin to enlarge, owing to the stress relief that must have occurred subsequent to crack initiation. This is particularly true of fine aggregate-paste cracks. Nevertheless as the load is substantially increased those fine aggregate-paste cracks which are properly oriented will begin to propagate. Their presence may still be overlooked when using conventional techniques owing to their smaller size. In the event that the specimen is not loaded to failure (in compression) these cracks may close (but not shorten) as a result of the stress being relieved. Even where failure has occurred, only a few cracks will exhibit extensive propagation and widening. Only those cracks which are oriented favorably, in maximum tensile stress fields, will coalesce and become part of the unstable crack network exhibited in conventional compression tests.

5.3 Other Findings

In addition to the principal findings outlined above, several other important observations were made. Among these was the determination that the paste-aggregate interface represents a weaker, more porous zone than occurs in the bulk. This porous space, occurring directly

behind the duplex film, basically originates from the poor packing of cement grains near the aggregates surface. Evidently the floc formed against the aggregate surface is fairly stable and is not much densified by vibrating the sample. This phenomenon is not due to the accumulation of bleed water under the aggregate. Indeed the specimens used in this research were prepared so as to avoid this defect. However it should be realized that the occurrence of bleeding in real systems is an additional cause of weakness in concrete.

As was noted in the very first figures presented, numerous small one-to-ten micrometer particles were found scattered about the substrate, subsequently the same phenomen was found on aggregate surfaces. Diamond (53) previously suggested that these were precipates from solution as a result of "constitutional supersaturation." However after considering the particle size analysis of Grindrod (67) and after inspecting these particles, some of which contained void interiors or interior voids and residual grains, Hadley's suppositions that these were the result of small particle hydration are seen to be correct.

Although the prior morphological conclusions of Hadley (20) have been confirmed in many particulars, the present results differ on certain points. Hadley did not mention the existence of the secondary $Ca(OH)_2$ layer. However its existence has been confirmed with all four cements and all three water:cement studied in this investigation. The suggested orientation of $Ca(OH)_2$ crystals in the residual cement shells has not been confirmed here. Rather the residual shells have been found by EDXA analysis to be composed of C-S-H gel typically having a C/S ratio less than three. The void space between the residual shell and the residual cement grain in a "Hadley grain" was described by Hadley as being bridged by acicular crystals. Only in a very few cases has this type structure been recognized in the present study. Instead, in almost every case, the void space was bridged by roughly hexagonal crystals generally oriented edge-on to the residual shell. Additionally Hadley failed to notice any "Hadley grains" existing away from the

paste-aggregate interface. Throughout this study such morphologies--residual shells, void space, residual grain--have been observed in all three specimen types with the various cements.

Finally, the findings reported herein appear to be characteristic of portland cement systems in general. Both the 0.50 and 0.65 water:cement ratios produced the same paste-glass interfacial morphology with all four cements. When 0.32 and 0.50 water:cement mortars were prepared the same morphology was again recognized, the only apparent difference being that the 0.32 w/c ratio mortar exhibited less void space near the aggregate interface than did the 0.50 w/c ratio mortar.

CHAPTER VI - CONCLUSIONS

It is concluded that:

1. The hydration pattern at interfaces is different from that in the bulk material and results in the presence of a structurally weak zone.
2. The path followed by cracks near paste-aggregate interfaces passes through different morphological elements depending on the age of the material.
3. Neither the type of portland cement nor the water:cement ratio significantly influence the morphology of the interfacial region or the crack pattern that develops.
4. A (roughly) 1 micrometer thick duplex film of oriented $Ca(OH)_2$ overlain with C-S-H gel is deposited on all surfaces in contact with the cement paste shortly after mixing. This film does not increase in thickness after its original deposition.
5. Occasional large well-formed $Ca(OH)_2$ crystals, having a thickness of about 2 micrometers and a maximum hexagonal face dimension of the order of 100 micrometers, are deposited edge-on to the duplex film as early as one day and extend from the bulk cement paste to the duplex film.
6. After several days a layer of secondary $Ca(OH)_2$, of usually thin oriented platelets, is deposited in available space between the duplex film and the overlying paste.
7. At one day cracks propagate primarily just above the duplex film through a porous zone that is relatively unfilled at this stage.
8. At about three days the cracks propagate either just above the duplex film or at the original interface.
9. At seven days or later, in systems of paste cast against flat glass plates, cracking occurs predominately at the

original interface. In mortars cracks undulate between just above the duplex film and the original interface. At this stage the secondary $Ca(OH)_2$ layer has bound much of the duplex film to the bulk cement paste.

10. Contrary to previous beliefs (that cracks initiate at about 30 percent of the ultimate compression strength level) it is concluded from micromorphological evidence that cracks in mortars and concretes are already present in portions of the paste-aggregate interfacial region at no load even prior to the drying of the material.

11. In compressively loaded mortars, cracks propagate within a zone typically within 30 to 40 micrometers of the paste-aggregate interface until a stress level near 100% of ultimate is reached, at which time the cracks start to propagate in an unstable manner through any portion of the system.

12. At least some cement grains, which are composed largely of C_3S, hydrate in a peculiar manner, yielding a residual shell of C-S-H gel separated by an intervening space from the residual unhydrated grain. As hydration proceeds the residual grain diminishes in size, but the shell does not increase in thickness. Occasional, mostly hexagonal-shaped crystals growing edge-to face-to each other, bridge or partly bridge the intervening space.

13. Recognition of this peculiar hydration pattern requires observation of broken grains. Fracture surfaces of interfacial regions exhibit many broken grains, almost all of which show this hydration pattern. Fracture surfaces of bulk cement paste regions exhibit far fewer broken grains; of these, most but not all show this pattern. The remaining broken grains exhibit the morphology of apparent inner and outer hydration product layers in contact with each other.

14. Despite the enhanced relative frequency of the grains showing the internal gaps between shell and residual grain near the interface, their existence does not significantly influence cracking near the interface, which is controlled by other structural elements previously described.

LIST OF REFERENCES

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1. Glanville, W., "Opening Address," The Structure of Concrete, Proceedings of an International Conference, Cement and Concrete Association, London, 1965.

2. Newman, K., "The Structure and Properties of Concrete--An Introductory Review," The Structure of Concrete, Proceedings of an International Conference, Cement and Concrete Association, London, 1965.

3. Feret, R., "On the Structure and Surface Condition of Inert Elements in the Concrete," Annales de l'Institut Technique du Batiment et des Travaux Publics, March-April, 1937.

4. Farran, J., "Mineralogical Contributions to the Study of the Adhesion Between Hydrated Constituents of Cement and the Imbedded Material," Revue des Materiaux de Construction et de Travaux Publics, (Paris). Nos. 490-492, 1956, pp. 155-172 and 191-209.

5. Lyubimova, T.Y. and Agapova, R.A., "Application of the Micro-Strength Method to the Structure of Set Cement Paste in Concrete," Beton i Zhelezobeton (7), pp. 299-303, 1959.

6. Lyubimova, T.Y. and Pinus, E.R., "Crystallization Structure in the Contact Zone Between Aggregate and Cement in Concrete," Colloid Journal (U.S.S.R.), V. 24, No. 5, 1962, pp. 491-498.

7. Slate, F.O. and Olsefski, S., "X-Rays for Study of Internal Structure and Microcracking of Concrete," Journal of the American Concrete Institute, V. 60, No. 5, May, 1963, pp. 575-587.

8. Hsu, Thomas T.C. and Slate, F.O., "Tensile Bond Strength Between Aggregate and Cement Paste or Mortar," Journal of the American Concrete Institute, V. 60, No. 4, April, 1963, pp. 465-485.

9. Hsu, T.T.C., Slate, F.O., Sturman, G.M., and Winter, F., "Micro-Cracking of Plain Concrete and the Shape of the Stress-Strain Curve," Journal of the American Concrete Institute, V. 60, No. 2, Feb., 1963, pp. 209-224.

10. Hsu, T.T.C., Microcracks Between Coarse Aggregate and Paste-Mortar in Concrete, Ph.D. Dissertation, Dept. of Structural Engineering, Cornell University, June, 1962.

11. Robinson, G.S., The Failure of Concrete with Particular Reference to the Biaxial Compressive Strength, Ph.D. Dissertation, Imperial College of Science and Technology, London, Nov., 1964.

12. Shah, S.P. and Chandra, S., "Critical Stress, Volume Change, and Microcracking of Concrete," ACI Journal, Vol. 65, No. 8, Sept 1968, pp. 770-781.

13. Hansen, T.C., "Cracking and Fracture of Concrete and Cement Paste," Causes, Mechanism, and Control of Cracking in Concrete, SP-20, American Concrete Institute, 1968, pp. 43-66.

14. Moavenzadeh, F., Kuguel, R., and Keat, L.M., Fracture of Concrete, Report R68-5, Dept. of Civil Engineering, Massachusetts Institute of Technology, March 1968.

15. McCreath, D.R., Newman, J.B., and Newman, K., "The Influence of Aggregate Particles on the Local Strain Distribution and Fracture Mechanism of Cement Paste During Drying Shrinkage and Loading to Failure," Materiaux et Construction, Vol. 2, No. 7, 1969, pp. 73-84.

16. Chatterji, S. and Jeffery, J.W., "Further Studies of the Three Dimensional Arrangement of the Hydration Products of Portland Cements," Indian Concrete Journal, Vol. 45, April, 1971, pp. 167-172.

17. Chatterji, S. and Jeffery, J.W., "The Nature of the Bond Between Different Types of Aggregates and Portland Cement," Indian Concrete Journal, Vol. 45, Aug., 1971, pp. 346-349.

18. Ash, J.E., "Bleeding in Concrete--A Microscopic Study," ACI Journal, Vol., 69, No. 4, April, 1972, pp. 209-211.

19. Farran, J., Javelas, R., Maso, J.C., and Perrin, B., "Etude de l'aureole de transition existant entre les granulats d'un mortier et la masse de la pate de ciment hydrate," liaisons de contact dans les materiaux composites utilises en genie civil, Vol. 1, R.I.L.E.M., Colloque International, Toulouse, France, 22-24 November, 1972, pp. 60-76.

20. Hadley, D.W., The Nature of the Paste-Aggregate Interface, Ph.D. Dissertation, School of Civil Engineering, Purdue University, November, 1972.

21. Schmittgrund, G.D., and Brown, S.D., "Bonding Efficiency Between Cement Hydrates and Steel," presented at the American Ceramic Society, 77th Annual Meeting, Cements Division, May 7, 1975.

22. Javelas, R., Maso, J.C., and Ollivier, J.P., "Realisation de lames ultra-minces de mortier pour observation directe au microscope electronique par transmission," Cement and Concrete Research, Vol. 4, No. 2, March 1974, pp. 167-175.

23. Richart, F.E., Brandtzaeg, A., and Brown, R.L., "A Study of the Failure of Concrete Under Combined Compressive Stresses," University of Illinois Engineering Experimental Station, Bulletin No. 185, Vol. 26, 1928.

24. Balmer, G.G., "Shearing Strength of Concrete Under High Triaxial Stress--Computation of Mohr's Envelope as a Curve," Structural Research Lab. Report, S.P. No. 23, Bureau of Reclamation, U.S. Dept. of the Interior, 1949.

25. Bellamy, C.J., "Strength of Concrete Under Combined Stress," Journal of the American Concrete Institute, Proceedings, Vol. 58, No. 4, October 1961, pp. 367-81.

26. Wastlund, G., "Nya ron Angaende Betongens Grand laggande Halbfasthelsegenskaper," Betong (Stockholm), Vol. 3, 1937.

27. Weigler, H., Beker, G., "Untersuchungen uber das Brach-und Verfarnungsverhallen von Beton bei zweiachsiger Beanspruchung," Vertrieb Durch Verlag von Wilhelm, Ernest & Sohn, Berlin 1963.

28. Weigler, H., Beker, G., "Uber das Bruch-und Verfarnungsverhallen von Beton bei mehrachsiger Beanspruchung," Der Bauingenieur, Vol. 36, No. 10, October 1961, pp. 390-6.

29. McHenry, D., Karni, J., "Strength of Concrete Under Combined Tensile and Compressive Stress," Journal of the American Concrete Institute, Proceedings, Vol. 54, April 1958, pp. 829-40.

30. Bresler, B., Pister, K.S., "Strength of Concrete Under Combined Stresses," Journal of the American Concrete Institute, Vol. 30, No. 3, September 1958, p. 321.

31. Bresler, B., Pister, K.S., "Fracture of Plain Concrete Under Combined Stresses," Transactions of the American Society of Civil Engineers, Vol. 122, 1957, pp. 1049.

32. Tsuboi, Y., Suenaga, Y., "Experimental Study on Failure of Plain Concrete Under Combined Stresses," Part 3, University of Tokyo, Feb., 1960.

33. Glucklich, J., "On the Compression Failure of Plain Concrete," Dept. of Theoretical and Applied Mechanics, Univ. of Illinois, T. & A.M. Report No. 215, March 1962.

34. Glucklich, J., "Static and Fatigue Fractures of Portland Cement Mortar in Flexure," University of Illinois, Illinois Cooperative Highway Research Program, Series No. 90, 1965.

35. Welch, H.B., Haisman, B., "The Application of Fracture Mechanics to Concrete," University of New South Wales, UNICIV Report No. I-12, Nov. 1968.

36. Welch, H.B., Haisman, B., "Fracture Toughness Measurements of Concrete," University of New South Wales, UNICIV Report No. R.42, January, 1969.

37. Naus, D., Rejali, H.M., Lott, J.L., and Kesler, C.E., "Cracking of Concrete," University of Illinois, Engineering Experiment Station Bulletin 504, 1970.

38. Nadeau, J.S., Mindness, S., and Hay, J.M., "Slow Crack Growth in Cement Paste," Journal of the American Ceramic Society, Vol. 57, No. 2, Feb. 1974, pp. 51-54.

39. Griffith, A.A., "The Phenomena of Rupture and Flow in Solids," Phil. Trans., Royal Society, Series A, Vol. 221, 1920, pp. 163-198.

40. Irwin, G.R., "Fracture Dynamics," Fracturing of Metals, American Society of Metals, Cleveland, Ohio, 1948.

41. Inglis, C.E., Transactions of the Institute of Naval Architects, London, Vol. 55, 1913, p. 219.

42. Abrams, D.A., Design of Concrete Mixtures, Chicago, Lewis Institute, Structural Materials Research Laboratory, Bulletin No. 1, Dec. 1918, p. 20.

43. Wischers, G., Effect of Temperature Variation on the Strength of Cement Stone and Mortar, Dusseldorf, Verein, Deutscher Zementwerke, 1961, p. 117.

44. Powers, T.C., Physical Properties of Cement Paste, National Bureau of Standards Monography no. 43, Vol. II, Washington, 1962, pp. 577-609.

45. Brandt, H., "A Study of the Speed of Sound in Porous Granular Media," Journal of Applied Mechanics, Vol. 22, No. 4, Dec. 1955, pp. 479-486.

46. Brown, C.B., "Models for Concrete Stiffness with Full and Zero Continuity," The Structure of Concrete, Proceedings of an International Conference, London, 1965, Cement and Concrete Association, 1968, pp. 3-15.

47. Mather, Bryant, Discussion of Reference (46), The Structure of Concrete, Proceedings of an International Conference, London, 1965, Cement and Concrete Association, 1968, p. 43.

48. Hansen, T.C., "Theories of Multi-Phase Materials Applied to Concrete, Cement Mortar and Cement Paste," The Structure of Concrete, Proceedings of an Internation Confernce, London, 1965, Cement and Concrete Association, 1968, pp. 16-23.

49. Hashin, Z., "Theory of Mechanical Behavior of Heterogeneous Media," Applied Mechanics Reviews, Vol. 17, No. 1, January, 1964, pp. 1-9.

50. Brunauer, S., "Tobermorite Gel--The Heart of Concrete," American Scientist, Vol. 50, No. 1, March, 1962, pp. 210-229.

51. Russ, J.C., Coordinator, Energy Dispersive X-Ray Analysis, STP 485, American Society for Testing and Materials, 1971.

52. Diamond, S., "Application of Scanning Electron Microscopy to the Study of Hydrated Cement," Third Annual Electron Microscope Symposium, Chicago, Ill., April 1970, pp. 387-392.

53. Diamond, S., "Identification of Hydrated Cement Constituents Using a Scanning Electron Microscope--EnergyDispersive X-Ray Spectrometer Combination," Cement and Concrete Research, Vol. 2, 1972, pp. 617-632.

54. Diamond, S., Young, J.F., and Lawrence, F.V. Jr., "Scanning Electron Microscopy--Energy Dispersive X-Ray Analysis of Cement Constituents--Some Cautions," Cement and Concrete Research, Vol. 4, 1974, pp. 899-914.

55. Chatterji, S. and Jeffery, J.W., "Three-Dimensional Arrangement of Hydration Products in Set Cement Paste," Nature, Vol. 209, March 1966, pp. 1233-1234.

56. Chatterji, S. and Jeffery, J.W., "Strength Development in Calcareous Cements," Nature, Vol. 214, May 1967, pp. 559-561.

57. A.S.T.M., X-Ray Powder Data File, American Society for Testing and Materials, STP 48-J, Vol. 4, 1960.

58. Mather, K., "Examination of Cement Pastes, Hydrated Phases, and Synthetic Products by X-Ray Diffraction," unpublished report, 1971.

59. Diamond, S., "CE-698--The Chemistry of Cement," Class Notes, School of Civil Engineering, Purdue University, Fall, 1974.

60. Williamson, R.B., "Solidification of Portland Cement," Report No. UC-SESM 70-23, University of California, Berkeley, 1970.

61. Taylor, H.F.W., ed. The Chemistry of Cements, Academic Press, London, Vol. 1, 1964, 460 pp.

62. Mills, R.H., "Collapse of Structure in Cement Hydrates," Technical Publication, The University of Calgary, Faculty of Engineering, July 1968.

63. Mills, R.H., "Collapse of Structure and Creep in Concrete," Technical Publication, The University of Calgary, Faculty of Engineering, April, 1969.

64. Diamond, S., personal communication, March, 1975.

65. Copeland, L.E. and Bragg, R.H., "Preparation of Samples for the Geiger Counter Diffractometer," Research Department Bulletin 92, Portland Cement Association, 1958, pp. 1-10.

66. Williamson, R.B., "Constitutional Supersaturation in Portland Cement Solidified by Hydration," Journal of Crystal Growth, Vol. 3, 1968, pp. 787-794.

67. Grindrod, P.S., "Application of the Andreason Pipet to the Determination of Particle Size Distribution of Portland Cement and Related Materials," Fineness of Cement, A.S.T.M., STP-473, 1970, pp. 45-70.

68. Lucchi, F.R., "Shrinkage Cracks on Frosted Surfaces of Desert Sand Grains," JEOL News, Vol. 9E, No. 1, 1971, pp. 18-19.

69. Krinsley, D.H. and Doornkamp, J.C., Atlas of quartz sand surface textures, Cambridge University Press, London, 1973.

70. Scholer, C.F., "An Investigation of the Bond Between Portland Cement Mortar and Coarse Aggregate," Ph.D. Dissertation, Purdue University, 1965.

71. Alexander, K.M., "Strength of the Cement-Aggregate Bond," Proc. American Concrete Institute, Vol. 56, No. 5, Nov. 1959, pp. 377-390.

72. Hirche, D. and Wolff, G., "Diffusion Und Ionenaustausch Bei Der Alkali-Kieselsaurereskton," Cement and Concrete Research , Vol. 4, 1974, pp. 609-621.

73. Dhir, R.K. and Sangha, C.M., "Development and propagation of microcracks in plain concrete," Materiaux et Construction, Vol. 7, No. 37, 1974, pp. 17-23.

74. Norton, J.T., "The Principles of the Radiographic Process," Symposium on Radiography and X-Ray Diffractions, Philadelphia, 1937, pp. 3-24.

75. Thornton, P.R., Scanning Electron Microscopy--Applications to Materials and Device Science, Chapman and Hall, London, 1968.

76. Richart, R.E., Brantzaeg, A., and Brown, R.L., "The Failure of Plain and Spirally Reinforced Concrete in Compression," Univ. of Illinois, Engineering Experimental Station, Bulletin No. 190, 1929.

77. Berg, O.Y., "K Voprosu O Prochnosti I Plastichnosti Betona," Dokbadi Akademi Nauk USSR, Tom LXX No. 4, 1950.

78. Jones, R., "A Method of Studying the Formation of Cracks in a Material Subjected to Stress," British Journal of Applied Physics, Vol. 3, 1959.

79. L'Hermite, "Present Day Ideas on Concrete Technology, 3rd Part, The Failure of Concrete," RILEM Bulletin No. 18, June 1954.

80. Hognestad, E., Hanson, N.W., McHenry, D., "Concrete Stress Distribution in Ultimate Strength Design," Journal of the American Concrete Institute, Vol. 27, No. 4, Dec. 1955.

81. Shah, S.P., and Winter, G., "Inelastic Behavior and Fracture of Concrete," Journal of the American Concrete Institute, Vol. 63, No. 9, Sept. 1966, pp. 925-930.

82. Moavenzadeh, F. and Bremner, T.W., "Fracture of Portland Cement Concrete," Int. Conf. on Structure, Solid Mechanics, and Engineering Design in Civil Engineering, Southhampton University, 1969.

APPENDIX

APPENDIX I

DETAILS OF SPECIMEN PREPARATION

AI.1 Type I Specimens

Type I specimens consisted of cement pastes cast against horizontal microscope slides. The slides were precleaned petrographic microscope slides measuring 27 x 46 x 1.2 mm purchased from Ward's Natural Science Establishment, Inc. The cement pastes were made from all four of the cements described in Table 2 at both a 0.50 and 0.65 w/c ratio.

AI.1.1 Glass Slide Preparation

Five hundred glass slides were initially purchased for this study. Ninety-five of these were selected at random as substrates on which cement would be cast. These were then laid flat on a cleaned vacuum-oven grate. The slides and grate were then removed to the vacuum oven and continuously evacuated at 110 C at a maximum vapor pressure of 100 micrometers of Hg for twenty-four hours. A liquid nitrogen trap was used throughout the evacuation period.

After evacuation the slides were placed in a vacuum desiccator. The bottom portion of the slides, having been in contact with the oven grate, was always kept downward. To separate the various layers of slides in the desiccator, clean weighing paper was placed between them. Once the slides were placed in the desiccator it was evacuated to approximately 100 micrometers of Hg and sealed.

AI.1.2 Cement Preparation

All the cements, at both water:cement ratios, were mixed according to A.S.T.M. method C-305 with the exception that the mixer's lowest speed was used. Only distilled water was used in the mixing.

The glass substrates were subsequently removed from their storage desiccator and individually placed flat with their bottom side down in

50 ml plastic weighing boats. The surfaces of the slides were blown with a blast of Freon gas to assure that no dust particles might have settled on them. The weighing boats containing the slides were covered with a fresh piece of aluminum foil to avoid dust collection. The slides were now ready for deposition of the cement paste.

The paste, having been thoroughly mixed, was pipetted from the bottom of the mixing pan onto the clean microscope slides. Only one slide was covered with paste at a time. Each time a new slide was covered with paste, the cement in the mixing pan was briefly stirred using the pipette. Never were two slides covered with paste without the pipette returning for fresh paste to the mixing pan. The pipette orifice was always submerged below the uppermost level of the paste being placed.

As each slide was completely covered with paste, it was removed to a plastic bag containing a weighing boat filled with water and another smaller weighing boat containing Mallcosorb (a CO_2 absorbent). At no time was the slide removed from its weighing boat container. After all the Type I specimens of a specific composition were prepared, the plastic bag containing them, the water, and the Mallcosorb was sealed with plastic tape. At no time did the paste cease to exhibit a glossy appearance. Thus indicating that only insignificant evaporation occurred during the placing process.

AI.1.3 Curing, Drying, and Storage

After the specimens were sealed in the plastic bag, they were allowed to cure for eight hours. Water vapor was observed condensing inside the plastic bag within about fifteen to thirty minutes of its being sealed. At the end of the eight-hour period, small holes were cut in the plastic bag above each Type I specimen. Through these holes each weighing boat was filled with aged saturated $Ca(OH)_2$ solution to above the level of the cement paste. No solution was allowed to impinge directly on the specimens. The specimens were allowed to cure under this solution at room temperature for varying lengths of time (from

1 to 28 days). The solution level was maintained above the specimens upper surface.

When a specimen had hydrated for the desired length of time, it and its container were removed to a nitrogen gas filled gloved box. Here the $Ca(OH)_2$ solution was poured off and the specimen was placed in a vacuum desiccator. For a period of three days the specimens were continuously evacuated. The evaporable water was collected in a liquid nitrogen cold trap which was cleaned from one to three times daily. At the end of three days the specimen was removed from the vacuum and placed in a desiccator containing enough $Mg(ClO_4)_2 \cdot 2H_2O$ and Mallcosorb to assure both a stable vapor pressure and a lack of CO_2. The specimens remained stored in this second desiccator for a period of not less than two weeks.

AI.1.4 X-Ray and SEM Preparation

After the specimens had been thoroughly dried they were prepared for X-ray diffraction and SEM analysis. The procedure generally followed the steps listed below.

1. The specimen was removed from the desiccator but still remained inside the nitrogen filled gloved box.

2. The bottom of the glass slide was marked with a wide black felt tip marker.

3. The two halves of the specimen, having spontaneously separated near the original interface, were wrapped in thin polyvinyl chloride (PVC) film.

4. Each of the two specimen halves were removed from the gloved box. The plastic film was thermally sealed.

5. Each half of the specimen was placed in the diffractometer. Usually the region between 5 and 55 was scanned, (copper radiation, $K\alpha$). The PVC film appeared only to diminish the X-ray intensity and not to alter the diffraction pattern.

6. After diffraction, the specimens were returned to the gloved box, where the PVC film was removed.

7. The glass slide was scratched with a diamond pencil about 15 mm from each end. Glue (Duco cement) was applied to a properly labelled aluminum SEM specimen stub. The glass slide was placed on the SEM stub and the two overhanging ends were broken off at the scratches. To guarantee that the bottom and top of the glass slide had not become interchanged, the previously applied black ink was observed to "run" in the glue.

8. The cement paste was prepared in the same fashion as the glass slide. However, the excess cement was removed by either breaking the ends of the specimen off in bending or by using a hammer and chisel.

9. Both halves of the specimen were removed to a small third desiccator where they were evacuated. When a sufficient number of specimens had accumulated (usually eight halves) the specimens were coated first with carbon and then with chromium.

10. After coating, the specimens were placed in a desiccator containing $Mg(ClO_4)_2 \cdot 2H_2O$ and Mallcosorb. This desiccator was then evacuated and sealed pending specimen inspection.

AI.1.5 Carbonation Evaluation

Initially it was feared that CO_2 in the atmosphere might cause carbonation of the cement hydration products and thereby possibly introduce unexpected artifacts. To avoid this type of contamination both Type I and Type II specimens were exposed to the atmosphere only sparingly. Only two opportunities existed for the introduction of CO_2 to the specimen surfaces: (a) during the transfer of the specimen to and from the coating apparatus and (b) during the transfer to and from the SEM.

To investigate the potential for carbonation several extra A6501 specimens were prepared as outlined above. The presence of CO_2 was evaluated by X-ray diffraction (carbonation) and infra-red spectrometry. Interface specimens were exposed inside the gloved box and in the laboratory atmosphere for 5, 20, and 60 minutes. In no case was any crystallographic change noted. All the specimens exposed inside the

gloved box showed no evidence of the CO_2 bond stretching band at approximately 1400 cm^{-1}. All the specimens exposed to the laboratory air showed the presence of CO_2 in their IR-patterns, the trend being progressive with longer exposure. Additionally several specimens which had been removed from the gloved box inside PVC bags showed no evidence of CO_2.

It is surmised from these results that when a dried specimen is exposed to the atmosphere, CO_2 (and other gases) sorb onto the extensive surface of the cement pastes. If the specimen is only briefly exposed, 5-20 minutes, no carbonation may occur. On extended exposure in moist conditions no evaluation could be made. No microstructural alteration is believed to have occurred as a result of carbonation in this investigation.

AI.2 Type II Specimens

These specimens were prepared by casting cement paste in cylindrical polyethylene centrifuge tubes measuring approximately 2.54 cm in diameter by 10 cm in length. The paste was obtained from the corresponding Type I specimen cement preparation. Paste was placed into the tubes in three layers with each layer vibrated for 15 seconds. The tubes were placed upright in 1,000 ml beakers containing approximately 50 ml of free water. The beakers containing the pastes, tubes, and water were then sealed with polyvinyl chloride film.

All Type II specimens were hydrated in the beakers for one complete day. At the end of this period the tubes were removed from the beakers and a small hole was melted into the closed end of the polyethylene tubes. The specimens were then immersed individually upside-down in boiling water. Owing to differential thermal expansion, the polyethylene tubes were easily removed from the pastes within one minute of immersion. After removal, the tube specimens were stored under $Ca(OH)_2$ at room temperature until a total curing time of 7, 14, or 28 days accrued. Drying and storage of these specimens was the same as for the Type I specimens.

Two methods of surface preparation were used. A few specimens were sawn in two at mid-height and polished on medium sandpaper to remove the saw marks. Most of the specimens were simply fractured with a hammer and chisel near mid-height. Those specimens which were polished were placed in PVC bags and X-rayed as discussed in section AI.1.4. SEM analysis showed that polishing introduced significant artifacts and was therefore discontinued. A complete discussion detailing the nature of the fracture and polished sections is presented in Chapter III.

AI.3 Type III Specimens

The Type III specimens consisted of mortars having w/c ratios of 0.50 and 0.32 and two volume fractions of ASTM designation C-109 Ottawa silica sand of 0.30 and 0.60. All specimens were prepared using cement "A" (Table 2). Mixing was conducted according to ASTM method C-350. The mortars were compacted in three equal layers into cylindrical polyethylene centrifuge tubes measuring 2.54 cm in diameter by 10 cm in length. Each layer was rodded with a glass stirring rod 25 times and vibrated for 15 seconds. When the tubes were filled they were covered with tight fitting polyethylene centrifuge tube caps having an approximate 1 mm diameter hole melted into the edge of the top of the cap. As the caps were pushed into place, the tubes were tilted so that any trapped air or liquid would escape via the hole. Once the air and liquid had escaped, the hole became sealed with mortar. Fourteen mortar specimens were prepared at a time. Usually a maximum of fifteen minutes elapsed between the beginning and end of the filling and compaction process.

During the filling process, all fourteen specimen tubes were held in a single styrofoam container. This container was especially fashioned to attach to a rotisserie device. Once the tubes were filled and capped, all the specimens and the styrofoam container were transferred to the rotisserie. Here the specimens were rotated in the vertical plane about their mid-heights for one day. The intention of this rotating

process was to avoid differential settlement or bleeding. Only the low w/c ratio, high sand volume-fraction specimens showed evidence of poor compaction. These specimens showed a maximum 3% variation in specific gravity from top to bottom. All other combinations exhibited specific gravity variations of 1% or less.

After one day of hydration in the polyethylene tubes the mortar was removed as described in section AI.2. The mortar was thereupon cured at room temperature under a saturated $Ca(OH)_2$ solution for an additional thirteen days. At the end of the hydration period, a total of fourteen days, the top and bottom of each cylinder was sawed away using a thin-high-speed-diamond blade petrographic saw cooled with tap water. The height of the remaining right cylinder was nominally five centimeters.

The sawed right cylinders were thereupon dried in a manner similar to the Type I and Type II specimens. After drying, the mortar specimens were subjected to 0 %, 30%, and 60% of their ultimate compressive strength. The ultimate compressive strength was taken as the average strength of four cylinders in each group which had been loaded to failure. The specimens subjected to failure load and to partial ultimate load were selected at random. No cylinder having obvious flaws was selected for analysis.

Once the specimen had been subjected to the desired load, it was fractured using a hammer and chisel at right angles to its long or loaded direction. This fracture surface was coated first with carbon and then chromium for SEM inspection. Storage, as with the other specimens, was over $Mg(ClO_4)_2 \cdot 2H_2O$ and Mallcosorb (a CO_2 absorbent).

APPENDIX II

DETAILS OF CALIBRATION CURVE PREPARATION

Calibration curves were prepared to allow the semi-quantitative analysis of microstructural features of interest. The original analytical scheme applied to cement compounds was devised by Diamond (53). In concept the approach is simple. By taking compounds of known stoichoimetry and subjecting them to EDXA analysis a series of coordinate points may be derived. These coordinates are composed of the X-ray $K\alpha$ ratios and the molar ratios of interest. Therefore it is obvious that the resulting curves relate X-ray intensities to molar composition. The numerical determination of elemental concentration was not attempted.

Three calibration curves were prepared:

(1) $CaK\alpha / SiK\alpha$ vs. CaO/SiO_2

(2) $CaK\alpha / SK\alpha$ vs. CaO/SO_3

(3) $CaK\alpha / AlK\alpha$ vs. CaO/Al_2O_3

The compounds used in the calibration are presented in Table AII-1. Each of the compounds was prepared by sprinkling several milligrams of the material onto an SEM specimen stub covered with double stick tape. These were then coated with a layer of carbon and chromium to prevent charging under the electron beam.

After the specimen was placed in the SEM it was observed at low magnification. Typically five or six particles oriented approximately perpendicular to the electron beam were selected for elemental analysis. The magnification of the instrument was then increased to assure that the electron beam would impinge only on the area of interest. Each of the five or six particles were subjected to analysis at two points on their surface.

EDXA analysis was conducted for either a duration of one hundred seconds or for a total integrated count of one hundred thousand. The

TABLE AII-1

Compounds Used in EDXA Calibration

Curve Description	Compounds Used	Oxide Ratios
$CaK\alpha / SiK\alpha$ Vs. CaO/SiO_2	βC_2S	2.0
	Tobermorite	0.835
	C_3S	3.0
	βCS	1.0
$CaK\alpha / SK\alpha$ Vs. CaO/SO_3	$CaSO_4 \cdot 2H_2O$	1.0
	$C_3A \cdot CaSO_4 \cdot 12H_2O$	4.0
	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	2.0
$CaK\alpha / AlK\alpha$ Vs. CaO/Al_2O_3	C_3A	3.0
	C_3AH_6	3.0
	$C_3A \cdot CaCO_3 \cdot 11H_2O$	4.0
	C_4AF	4.0
	C_4AH_{13}	4.0
	$C_4A_7CaF_2$	1.714
	$C_3A \cdot CaSO_4 \cdot 12H_2O$	4.0
	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	6.0

data was then stripped of background using the Nova 1200 computer, and the respective integrated Kα counts recorded. Typically a minimum of 40,000 counts remained after the background had been removed. In the event the reader would like to analyze this data for himself, Table AII-2 presents the accumulated raw data. After those data were collected the respective curves were plotted and a least squares "line of best fit" drawn through the points.

TABLE AII-2

Accumulated Calibration Data

(a)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	Si
βC_2S	1	79493	49770	16948
	2	79955	50282	17974
	3	77907	49585	17801
	4	74387	48013	15741
	5	77952	49950	17002
	6	71130	45074	15298
	7	80488	50713	17257
	8	73304	46115	16862
	9*	71749	48523	12118
	10*	59085	39851	10017

[1]Total Counts Remaining After Background Subtract

*Not Included in Curve Fit Procedure

TABLE AII-2 (Cont.)

(b)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	S
$CaSO_4 \cdot 2H_2O$	1	49370	17999	18391
	2	61539	22516	23067
	3	53882	19801	19534
	4	52551	18745	18841
	5	48237	17931	17479
	6	62991	22937	22784
	7	54666	19804	20587
	8	50595	18795	17561
	9*	54046	19289	20116
	10*	51314	18706	18055

(c)

			Ca	Al
C_3A	1	73115	45363	12097
	2	75509	46387	12027
	3	67501	42533	11246
	4	70096	41884	11920
	5	61466	36486	9698
	6	63000	37811	10834
	7	70591	41993	11191
	8	62117	38260	9123
	9*	53019	35305	4616
	10*	62145	38612	7982

[1]Total Counts Remaining After Background Subtract

[2]Not Included in Curve Fit Procedure

TABLE AII-2 (Cont.)

(d)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	Al
C_3AH_6	1	39516	23617	4975
	2	38740	23282	4906
	3	45151	27002	6193
	4	45101	27394	5638
	5	41147	25361	6060
	6	43998	26732	6080
	7	41125	25318	4862
	8	44205	26199	7084
	9	46172	26233	7876
	10	44404	25973	7759
	11	47240	28738	8345
	12	40709	23740	7072

(e)

			Ca	Si
Tobermorite	1	54211	19707	21625
	2	48329	18131	17962
	3	32016	12872	8480
	4	33147	12773	8310
	5	22986	5561	6375
	6	16182	2927	4561
	7	50718	16098	20134
	8	50413	16611	19236
	9	45222	17635	15315
	10	56706	20487	22260
	11	49731	16339	20743
	12	47269	13505	19540

[1]Total Counts Remaining After Background Subtract

TABLE AII-2 (Cont.)

Compound	Point No.	Total Counts[1]	Kα Counts		
			Ca	S	Al
(f)					
$C_3A \cdot CaSO_4 \cdot 12H_2O$	1	41007	21133	5649	3708
	2	49119	25059	5736	3992
	3	48225	23623	6175	5372
	4	43762	23471	4709	4495
	5	47100	25223	4579	4943
	6	51189	26905	5298	4484
	7	43265	23208	4967	2676*
	8	42822	22932	3542	2153*
	9	54919	27346	7204	5134
	10	45155	24000	4451	4620
(g)					
$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	1	32334	12450	5815	1700
	2	38242	17909	8321	2379
	3	40870	20368	2045*	2172
	4	38850	18545	7328	2370
	5	32822	15364	7135	1929
	6	36708	16424	8221	1815
	7	33954	16502	6639	1735
	8	38994	16715	8062	2153
	9	39400	16792	8015	2376
	10	43811	20440	9590	2563
	11	44727	21559	9615	2154
	12	36459	15560	8416	2264

[1]Total Counts Remaining After Background Subtract

[2]Not Included in Curve Fit Procedure

TABLE AII-2 (Cont.)

(h)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	Al
$C_3A \cdot CaCO_3 \cdot 11H_2O$	1	42408	24799	4602
	2	34348	20834	3466
	3	34577	18937	5358
	4*	30858	19844	1707
	5	32600	17192	3720
	6	31269	16955	3856
	7	38576	21493	4865
	8	36209	21214	3634
	9	38913	20798	5140
	10	36195	21513	3348
	11	29718	16133	3177
	12	28797	14696	3267

(i)

Compound			Ca	Si
C_3S	1	70996	46565	7907
	2	65212	42648	6967
	3	51701	31677	6461
	4	66654	40651	8518
	5*	77368	50675	6203
	6*	70316	43905	9057
	7	70316	43905	9057
	8	68026	43662	8801
	9	66006	41219	9046
	10	69475	44201	8934

[1]Total Counts Remaining After Background Subtract

*Not Included in Curve Fit Procedure

TABLE AII-2 (Cont.)

(j)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	Al
C_4AF	1	51808	25504	3240
	2	53745	26909	3457
	3	56904	27237	5007
	4	52163	25513	3679
	5	50824	24722	2678
	6	58274	27723	3425
	7	58205	28566	4410
	8*	55084	28067	2542
	9	53303	26753	3431
	10*	50663	26068	2197

(k)

			Ca	Al
C_4AH_{13}	1	42452	25741	5328
	2	46265	27530	6592
	3	32574	18426	3526
	4	37292	21492	3725
	5	40611	24035	6151
	6	43604	26201	5546
	7*	33072	5329	19624
	8*	31757	4359	19988
	9	44251	23224	7279
	10	43919	25052	5202

[1]Total Counts Remaining After Background Subtract

*Not Included in Curve Fit Procedure

TABLE AII-2 (Cont.)

(l)

Compound	Point No.	Total Counts[1]	Kα Counts	
			Ca	Al
$C_{11}A_7 \cdot CaF_2$	1	50966	27420	11067
	2	53038	26907	13752
	3	46049	21907	12579
	4	49815	25312	13507
	5	52846	27770	14611
	6	54667	26382	16055
	7	49933	25495	13292
	8	55692	27527	15044
	9	45662	23426	11559
	10	55595	27043	15470

(m)

			Ca	Si
βCS	1	39962	21951	11896
	2	59428	32812	17785
	3	95604	45513	35241
	4	93152	44150	36047
	5	67750	33154	25862
	6	61271	29610	23794
	7*	29259	18507	5090
	8	41211	23955	10615
	9	53902	27614	19042
	10	48307	25047	17277
	11	52700	25634	20275
	12	53870	25305	21469

[1]Total Counts Remaining After Background Subtract

*Not Included in Curve Fit Procedure

APPENDIX III

Chemical Analysis of Cements

Designation	A	B	C	D	#317
Description	Type I, High Alkali	Type I, Low Alkali	Type IS	Type V	Type I, Used by Hadley
Blaine cm^2/gm	3510	3670	5700	4090	3380
CaO	62.95	66.08	64.61	65.52	65.30
SiO_2	20.81	20.86	21.21	22.67	21.76
Al_2O_3	5.42	5.03	5.35	3.51	5.41
Fe_2O_3	3.02	2.48	2.75	2.82	1.97
MgO	2.80	1.16	3.55	1.21	1.11
TiO_2	0.22	0.27	0.00	0.29	----
SO_3	3.01	3.02	2.38	2.12	2.43
K_2O	0.81	0.41	0.08	0.21	----
Na_2O	0.16	0.04	0.03	0.23	0.38[2]
Water Soluble Alkalies % Na_2O/K_2O	$0.11/0.62$	$0.016/0.215$	$0.01/0.014$	$0.02/0.042$	----
LOI[1]	0.81	0.65	0.04	1.32	1.78
C_3S	48.82	64.62	55.19	60.83	51.20
C_2S	22.82	11.04	19.17	19.10	23.83
C_3A	9.27	9.13	9.54	4.51	11.00
C_4AF	9.18	7.53	8.36	8.60	5.99

[1]LOI = Loss on Ignition

[2]Total Alkalies Expressed as Na_2O

APPENDIX IV

RAW EDXA DATA

Figure No.	Specimen Code	No.	K-Alpha Counts[1] Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
6	A5001G2	1		338	392	42485			384	172	
7	A5001G3	1	438	178		36957		268	11232	242	
8	A5001G4	1	466	252		39057		302	11018	138	18
16	D5001G3	1	384	132	272	27815	32	216	6762		
19	A5001P5	1			64	756	338		47995	106	68
		2				934			49428	88	
20	A5001P2	1			32	926	40		49684	24	
		2			30	2386	274		48266	74	116
23	C6501P1	1				644	134		49834	100	
25	G1B	1			1420	236			25740		
26	G4/24B	1			132	218	108		34880		
		2			158	1054	220		32454		
27	G1C	1			837				11818		
		2			710				11765		
		3			766	36			12012		
28	A5001G6	1		156	228	13882	324	32	35376	226	80
30	B5001G2	1			246	15243	366	134	34032	76	232
		2	96	42	107	22840	392		24800	265	44
31	C5001G3	1	668	364	1796	39050	182	218	4839	78	
32	C5001G4	1	118	82	445	16732	478		30656	252	87

[1] A blank implies no counts for that element.

APPENDIX IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
33	C6501G2	1	658	204	1785	41772	456	312	9346	96	
		2	658	302	1548	40083	580	420	10106	26	
		3	736	292	1335	43876	112	502	8171	90	
36	A5001P4	1		142		8916			41846	26	22
		2		64	241	9645	796		38219	90	218
37	A5001P3	1		76	45	8486			44701	18	94
		2		196	116	8263	406		41417	142	224
		3			124	3119	200		44174	176	46
38	A6501P7	1	18		57	9385			42367	18	108
		2		262	202	9017	444		42474	162	
39	A6501P2	1			437	11683	578		34774	202	204
		2		78	604	10918	922		36693	200	252
		3		110	854	9722	1906		36649	142	250
40	A6501P1	1			95	7543			45461	126	
		2				1996	140		46811	24	
42	B5001P3	1			204	8668	186		40867	104	132
		2			331	9241	1155		35509	276	320
43	B6501P3	1			221	8634	484		38551	158	166
		2			652	5461	1451		38397	121	1696

APPENDIX IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts								
			Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
44	B6501P2	1			191	7978	308		43803	48	94
		2			446	9039	1230		38933	132	150
46	C5001P4	1			148	11967	140		38239		112
47	C6501P2	1		118	154	9646	272		38430	243	144
		2		192	258	8411	697		39228	204	317
48	C6501P3	1		188	161	8167	646		41694	136	206
		2		240	318	9530	1226		35375	486	390
49	D5001P2	1				7822	108		43838	163	120
		2				8397			44097	18	22
		3		26	144	9290	374		40722		303
		4				1042	188		51688		
		5		24		8797			44100		22
		6				9174	420		42314	24	52
		7		24	51	9257	154		43537	48	36
		8			74	9760	370		40680	105	96
50	D5001P3	1		52		7788	32		44710	52	72
		2		1046	378	6980	1196		35420	100	1619
58	A5003G2	1		147		84			3422	20	14
		2				114			4724		
61	R23A	1			48	18			2932		

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
65	A6503G1	1		64	428	1792	234		54267	26	
68	B6503G7	1	24	18		3539			1183	10	
69	B6503G6	1				3351			1072	4	
72	C6503G1	1	30	38		3297			747	4	
73	C6503G2	1	22			3054	8		1297	8	
		2	8			3986			668	4	
		3				4025			769		8
		4				3456			542		
		5	24			3449			850		
		6	22	16		2980			1129	18	
		7				2534		28	484		
77	D6503G3	1		76		30909		248	9687	26	
78	A5003P1	1				408			45481		
		2				3409		78	41809		
		3	1580			1602	126		44420		18
		4	2361		2582	2098	3315		32219	24	178
		5	2697		2059	3080	2838		32433	80	106
79	A5003P2	1			351	6400	1042		34660	24	508
81	B6503P2	1				130	126		51663		
		2			26	1332			48513		

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
82	C6503P6	1				450			44238	62	
		2				834	78		44550	110	
		3			78	5934	464		38930	119	92
		4		128	270	4096	755		35274	164	708
85	D6503P4	1				8	16		4556		4
		2				64	8		4258		4
		3				271			3728		8
87	D6503P7	1		32		7660	164		39630	48	200
91	A5014G2	1	612	202		43084		388	6529		
		2		174	212	18361	520		26819		269
		3	624	118		33211	194		16849	50	
		4	521	168		32776		138	14184		48
92	A5014G1	1		64		31462		38	14303		
94	A5014G5	1	649	160		40292		270			
95	A5028G1	1	610	166		42563		278	5906	50	24
		2	716	292		42576		309	6707	26	
96	A5028G2	1	502	171		42839		360	6608		
98	B5007G2	1	29	168		36164		334	10387		
100	B5007G5	1	390	38		36886		302	11719	26	

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
102	B5028G1	1	792	150		40467		338	6062		
		2	608	148		42765	32	396	6650		
103	B5028G2	1	831	194		42033		308	6610		
109	C5014G2	1	650	178		42936		318	6260		
		2	639	190		42420		376	6068		
111	C5028G1	1	622	234		43772		304	6501		
		2	704	224		39477		306	6192		
112	C5028G2	1	519	170		40897		336	6893		
113	C5028G3	1	603	212		40836		312	6463		
117	D5028G1	1	572	238		42883		288	6496	26	
		2	655	168		40546		276	6192		
118	D5028G2	1	518	104		41242		358	6627		
122	A5007P9	1				2841	38		46648		24
		2			1709	1925	3479		37661		98
		3		156	89	5884	470		39968		530
		4				974			49417		
		5			1733	1090	3205		39629		
		6			482	3657	1510		41513		250
124	A5014P2	1			266	6820	957		39118		567
		2				716			47245		

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts								
			Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
126	A5028P3	1		220	328	5770	515		35136	84	588
		2				1721			47056		
128	A5028P2	1		34	312	5828	667		34340		1829
131	B5007P3	1			224	10096	308		34771	22	76
		2			4100	680	5594		33523		
		3		26	320	9701	532		37187	54	242
132	B5007P4	1			103	4740	556		43245		120
		2				496	32		45738		
		3				3052	415		44645		138
		4				372	116		49461		
133	B5014P2	1				3370	306		45251		
136	C5007P2	1				4286	300		45303	48	52
		2				741			46046		
		3				3232	132		44773		24
		4				396			47335		
139	C5014P2	1		140	170	5672	644		38465	60	276
		2				977			47287		
140	C5028P1	1			32	3607	529		42669	118	216
		2				952	130		46664		

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts								
			Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
143	D5007P6	1				3161	514		47032	24	224
		2				834			47725		
		3				3382	628		42664	48	331
		4				871			49139		
144	D5014P1	1				2856	411		4280		183
		2				675	78		49418		22
145	D5028P1	1			31	3705	373		43709		172
		2				2231	92		45737		78
156	A5003C2	1			80	7576	640	324	38644	24	82
		2			98	8440	488		37909	82	166
		3			342	7171	900		35863	24	710
164	A5028C3	1			439	9572	751	220	33171	84	56
		2				650	154		46315	80	
165	A6501C3	1			24	567	230		52093	50	118
		2			310	3950	948	366	43507		515
		3		44	350	5865	1202	316	40517	106	298
		4		78	4240	1920	272		36524		3970
		5			406	3511	1198	440	44282	26	373
		6			366	5776	890	338	41728	50	217

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts								
			Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
166	A5014F4	1			4	116			2059	8	18
		2				216	74		47985	82	124
175	A5003F4	1	8		169	88	132	25	1179		
177	C6503F4	1		64	406	13119			30401	132	22
		2		46	1559	12014			28837	64	140
		3		218	537	8898			27105	247	552
178	A5007F1	1			472	9437	731		34450	24	176
180	A5014F1	1				178	116		51819		
181	A5014F2	1		338	1147	7211	1610	252	31103		286
		2		116	381	10847	726	316	33345	146	277
182	A5028F1	1				2125	204		43695	132	48
		2				1056	346		46341		
183	A6501F5	1		16.	16	464	16		4147	14	
		2		153		382	42	12	2862		34
185	A6501F3	1				84			2918		
186	A6503F1	1				770			44935		18
190	B5003F6	1				598			1925		
192	C5003F1	1	1646			419			3010		
193	C5003F2	1				644			3860		
195	C5003F4	1	381			85		16	1085		
197	D5003F3	1		6		619			2943	4	4

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts								
			Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
203	Sand--2	2				57166				48	
		4				34444			1497	26	
		5				10328			78	14	
204	Sand--3	1				44912					
		2			2595	42218					
214	1-0.00-1	1				54872			3691		
		2				56229			1987		
		3				58128			1348		
		4				53589			3875		
		5				54488			2933		
220	1-0.00-12	1			192	575	170		51034		24
		2			70	898	172		46633	24	66
		3			128	752			45926	24	
		4			240	2197	361	202	42164	90	24
221	1-0.00-14	1		36	232	3099	764	376	41100		241
		2			206	1456	338		42060		180
		3			444	3412	685	328	38481	48	308
226	1-0.30-4	1				39572		166	7584	24	18
227	1-0.30-5	1				32890			1816		

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
232	1-0.30-3	1				1633	363	588	33257	22	80
		2				2236	637	1295	35045		247
		3				1945	254	142	42199		
233	1-0.30-1	1				989	382	242	42051	24	
		2				1998	435	520	40857		24
237	1-0.30-10	1				57304			474		
239	1-0.60-3	1		68		8938			33530		96
		2		356	1293	20276	341	806	13441	44	318
		3				47062			1506		
		4				49182			881	42	
242	3-0.00-6	1				26282	102		14463	175	
246	3-0.00-1	1			197	7152	665	48	30811	70	128
248	3-0.00-13	1	366			1665	118		42450	58	
		2						205	42101		
249	3-0.00-14	1				1275			41672		
		2			30	218			43785	50	
		3			187	310			45607		
252	3-0.00-5	1				18630	268		23866	183	64
254	3-0.30-2	1			148	10109	586	78	30043	24	189

Appendix IV (Cont.)

Figure No.	Specimen Code	No.	K-Alpha Counts Na 1.08	Mg 1.27	Al 1.50	Si 1.77	S 2.34	K 3.31	Ca 3.71	Mn 5.94	Fe 6.40
259	3-0.30-8	1				640			42877	48	
		2			22	2930	495	556	37928		30
		3			44	998	26		42903		
260	3-0.30-1	1				9604	258		31449	24	
		2				33750	190		14019		
		3				2879	322		37734		26
264	3-0.60-1	1			44	1648	138		35507	18	
265	3-0.60-3	1			664	15042	1026	226	18244	114	116
266	3-0.60-4	1			266	3807	1395	525	28193	24	248
267	3-0.60-5	1		120	558	7131	1375	557	25080		564
275	MA3201-3	1				49958			2038	24	

APPENDIX V

Literature Review of Failure Theories, Fracture Mechanics, and Composite Materials as Applied to Concrete Systems

AV.1 Introduction

Many theories treating the behavior of concrete have been advanced. Some of these deal with the strength properties of the material; others with its volume stability properties.

Feret (1) probably suggested the earliest (1897) strength theory for cement and concrete. He suggested that the strength of cement and concrete could be predicted by the following function:

$$S = f(V_c/(V_w + V_v))$$

where: S = strength

V_c = volume fraction of cement

V_w = volume fraction of water

V_v = volume fraction of voids

Since Feret's early work, additional research has led others to put forth other postulates. Among these were Wischers (2), Powers (3), and Abrams (4). Abrams' work resulted in the now generally accepted inverse relationship between w/c ratio and compressive strength:

$$S = A/B^x$$

where: S = strength at 28 days

A = 14,000 psi

B = 7

x = water/cement ratio by volume

Both Powers and Wischers continued this line of investigation. Powers suggested that the crushing strength of cement paste and mortar could be predicted by the equation:

$$S = AX^n$$

where: S = crushing strength

A = a characteristic strength of the cement gel, 13,000 psi to 18,500 psi

X = gel/space ratio

n = constant, typically 3

However it was observed by Wischers that when cement paste is moulded under pressure at very low w/c ratios, (less than 0.10) very high strengths result which may be predicted by:

$$S = 44{,}100\ V_s^n$$

where: S = strength in psi

V_s = volume fraction of solids

n = constant, typically 2.7

In addition to these strength prediction theories, procedures have also been suggested for the prediction of other important properties. Some of these have dealt with (a) drying shrinkage (5-9), (b) thermal coefficient of expansion (6, 10), (c) creep (11-13), and (d) elastic modulus (14-21). Within this review however, only those discussions dealing with strength or elastic modulus will be presented.

Even though this appendix is strictly a literature review* of what might be termed the megascopic properties of concrete, one point regarding microstructure should be borne in mind:

> "...a knowledge of the internal structure of any material is essential if its complex mechanical behavior at the phenomenological level is to be properly understood" (25).

At the time much of the work cited herein was accomplished this internal structure, at least on the microscopic level treated in the main text of this thesis, was not well defined. Hence the details of many of the theories do not agree with the true structure of the material they attempt to represent. It is hoped that the reader will realize that at present the two levels of materials research, microscopic and phenomenological, have not coalesced into a unified understanding of concrete. Rather, the two are still somewhat disjointed. Nevertheless, an appreciation of the material properties can be attained only from a review of the phenomenological research and a comparison with the microstructural findings.

* Three references have served as guides for this review (22-24).

AV.2 Classical Failure Theories

In order for reliable construction to be undertaken it is necessary to be able to predict the conditions under which failure will occur. Early in the history of construction, various engineers sought to derive theories which would allow the prediction of failure loads. These theories, usually based on the theory of elasticity and having some empirical components, are generally known as classical failure theories (26). In general they are phenomenological in nature.

Common assumptions for these theories require that the material be homogeneous, isotropic, and elastic up to some critical stress level (27). Upon realizing that materials are subjected to complex states of stress it became necessary to formulate the interrelationships of these stresses on the material. To this end, Robinson (22) has listed seven classical failure theories which attempt this interrelationship:

1. maximum principal stress theory (28)
2. maximum principal strain theory (28, 29)
3. maximum shear stress theory (30)
4. internal friction theory (31)
5. Mohr's theory (31)
6. octahedral shear stress theory (31) and
7. energy theories (32).

Rather than discuss the details of each theory, the reader is directed to the references noted with each theory or to Tettlemen and McEvily (33) for a short presentation. A brief analysis shows that all of those theories enumerated above may be expressed in the form

$$f(\sigma_1, \sigma_2, \sigma_3) = K$$

where σ_1, σ_2, and σ_3 are principal stresses and K is a constant for the given material. This provides a key to the comparative value of each theory for judging the applicability of any one strength theory for a specific concrete mix. This simply means that if the failure theory is applicable, K should remain constant for a concrete of constant mix proportions, components, and curing.

To test the classical failure theories Robinson (22) gathered the concrete strength data of several researchers (33-43). This included the results of 516 specimens from 43 different mixes. His findings were that none of the seven classical failure theories were generally applicable to concrete in complex states of stress. In several instances the theories predicted the qualitative failure mode but did not furnish suitable quantitative information.

In addition to the classical failure theories, several theories based on the theory of elasticity and empirical evidence have been proposed specifically for concrete. Among these are:

(a) the octahedral shear and normal stress theory proposed by Bresler and Pister (44),

(b) the internal friction-maximum stress theory proposed by Couard (45), and

(c) the Brandtzaeg theory (46).

Both (a) and (b) can be shown to reduce to the classical failure theories. Hence neither of these qualifies as a suitable failure criteria for concrete.

Brandtzaeg's theory is unique in that it considers concrete as a non-isotropic material consisting of a continuous array of crystals. These crystals are considered to be identical in their physical properties and to differ only in the orientation of their planes of weakness. A description of Brandtzaeg's theoretical material follows:

> As the load on the material "is increased it will be shared equally by all the elastic elements until at a certain load the most critically oriented plane of weakness will reach its elastic limit and slide. For any element this failing load is determined by Coulomb's internal friction theory... When this load is exceeded, the critical element will pass into a plastic state, but the deformation of this plastic element is limited by the remainder of the still elastic continuum. When a sufficient number of the elements become plastic due to further increases in obstructing elements, Brandtzaeg refers to this state as 'disorganized.'
>
> "Tensile failures are also permitted. A tensile failure will occur when the limiting tensile strength of an element

> is exceeded, the failure occurs normal to the tensile strain regardless of the orientation of the element's plane of weakness.
>
> 'With this as a basis, Brandtzaeg used statistics and calculus to derive lengthy equations which govern the failure of a cylindrical specimens for triaxial states of stress in which $\sigma_2 = \sigma_3$" (22).

Initially this theory is appealing because it treats concrete as a non-isotropic material. The theory is successful in predicting the stress-strain curve of concrete up to the internal micro-cracking stage. At that point the theory begins to fail.

Several reasons for this failure exists:

1. The theory does not recognize the inhomogeneity of concrete.
2. It fails to realize the variable modulus of elasticity.
3. The theory fails to recognize the structure and properties of the cement paste phases.

Nevertheless Brandtzaeg's theory is more qualitatively appealing than the other classical theories. In some cases where $\sigma_2 = \sigma_3$ the theory is quantitatively reasonable. However the suitability of this theory is no better than the best of the other classical theories.

AV.3 Fracture Mechanics Applied to Concrete

Fracture mechanics began as a distinct field of investigation upon the realization that many materials often failed below their conventionally determined failure strength. For example it was observed that occasionally steel plate having a high yield strength would fail at a much lower average stress level. In order to explain this type phenomena Griffith (47) and Inglis (48) postulated that material strength is subject to the flaws inherent in the production of the material or in its fabrication.

Inglis first suggested that flaws in a material acted as stress concentrations. In his analysis he assumed the limiting case of an infinitely thin crack of elliptical geometry existing long axis perpendicular to an applied tensile stress field. His analysis showed that for a crack having a half-length of "C" and a crack tip radius of

" ρ " that the actual stress at the crack tip in a plane stress field was given by

$$\sigma_{actual} = \sigma_{applied}\left[1 + 2\sqrt{c/\rho}\right]$$

Griffith, seeking to explain the catastropic failure of materials containing flaws thermodynamically suggested that the strain energy release rate resulting from a propagating crack should exactly equal the rate at which energy is required to create new surface as a result of the cracking. This concept worked extremely well for brittle materials such as glass. Griffith's analysis resulted in the following equation for an elliptical crack such as the one suggested by Inglis in a plane stress field.

$$\sigma = \sqrt{\frac{2E\gamma}{\pi c}}$$

where: σ = ultimate applied stress
E = modulus of elasticity
γ = specific surface of the material
c = one-half the crack length

This postulate works well for brittle materials such as glass but not for materials exhibiting energy dissipation or absorption mechanisms other than that required for the creation of new surface (e.g. plastic work).

Further interest in the application of fracture mechanics to structural materials was exhibited by Irwin (49) in his use of Westergaard's (50) stress functions and the accompanying stress intensity factor. As a result of this analysis Irwin was able to relate the stress intensity analyses of Inglis and Westergaard to the thermodynamic analyses of Griffith. His approach led to the following relationship:

$$G = \frac{\pi\sigma^2 c}{E}$$

where: G = strain energy release rate

If one assumes that the only energy absorbing mechanism available in fracture is the creation of new surface then $G = 2\gamma$, resulting in Griffith's equation. On the other hand if one notes that other energy absorbing processes exist then $G \neq 2\gamma$ but includes the surface energy term as an additive term to the required plastic work, i.e. "G" represents all the energy absorbed whether the material is brittle or plastic.

All three of these approaches may be related by the stress intensity factor, K. K may be defined as

$$K = \frac{\sigma_{actual}}{\sigma_{applied}} .$$

Additionally Inglis derived an equation

$$K = \sigma_{applied}\sqrt{c/\rho}$$

for the elliptical crack problem he considered.

Concrete researchers sought to apply the principles of fracture mechanics. However, the research has followed many different approaches. Often the Irwin, Griffith, and Inglis theories have been interchanged and interrelated primarily through the use of K, the stress intensity factor. Much of this work has been disappointing. The obvious reason for this disappointment is that concrete does not meet the assumptions of these theories. It is not homogeneous, isotropic, elastic, or continuous. Even with these shortcomings a useful characterization of a particular concrete mix might be obtainable if only one of the three approaches mentioned were used. However, researchers have tried to equate the three approaches using the K factor. It does not seem reasonable that one should be able to relate three theories which are based on linear elasticity with a material which at the phenomenological level is non-elastic and non-linear in response to load.

Notwithstanding, Glucklich, Naus, Kaplan, Moavenzadeh, and others have attempted to apply fracture mechanics to concrete. Naus et. al. (51) and Kaplan et. al. (52) have used concrete beams in third point bending

with carefully prepared notches to measure the parameters K_c' and G_c respectively. Recognizing that K is not a linear elastic parameter for concrete Naus et. al. chose to use K_c', meaning a critical stress intensity factor for a particular concrete. Kaplan measured values of G_c for concrete and allowed this parameter to account for all forms of energy absorbed in the failure (fracture) process.

Moavenzadeh et. al. (23) seeking to determine the interchangeability of the various fracture mechanics parameters determined the surface energy, γ, by the Nakayama method (53), K_c according to Lott and Kesler's method (54) and G_c according to Kaplan for several concretes, mortars, and pastes. When these parameters were converted algebraically to the same basis, γ, only very poor agreement was attained. For example at 28 days the γ-values obtained for concrete were 0.0200, 0.0273, and 0.0357 in. lb./in.^{2} from the Nakayama, Kaplan, and Lott and Kesler techniques respectively. If no other conclusions may be drawn, at least it should be obvious that the values of γ, K_c', or G_c are technique dependent. However, this alone does not negate the qualitative value of the fracture mechanics approach.

Naus et. al. evaluating K_c' for various concrete mix proportions concluded that:

> "varying the coarse aggregate content or gradation of coarse aggregate, or type of coarse aggregate" can influence the resistance to crack propagation in concretes (51).

In addition they published several figures showing the relationship of various mix properties to K_c', which might prove helpful from a design point of view.

Glucklich (55, 46) has contributed much to the application of fracture mechanics (G_c) to concrete in compression. Noting that cracks propagate parallel to a compressive stress he proposed the following fracture equation for concrete.

$$G = \frac{\pi b \sigma^2 \text{ compression}}{2E}$$

where: b = one-half the semi-minor axis length of an elliptical flaw whose major axis is parallel to the applied stress

He further illustrates that no critical size flaw may exist in a compression field. Glucklich argues that crack propagation to failure in concrete is a stepwise function consisting of at least two phases: slow crack growth and rapid crack growth. Additionally, he points out that concrete in conventional compression is subjected to shear and to dynamic loading as a result of the end constraint of the compression specimen and as a result of the rapid release of stored energy in the testing machine.

AV.4 Composite Materials Aspects of Concrete

Little work other than that noted in section AV.1 has been reported treating the strength of concrete from a composite materials point of view. Ishai (57) reported in 1961 that increasing the volume fraction of sand in a mortar (w/c = 0.32) led to an increase in flexure strength. The sand volume fractions investigated ranged from 18% to 80% of the total volume. A volume fraction of 36% of sand yielded the highest flexural strength. Neither a statistical nor a microstructural investigation was performed in this study.

In contrast to the limited composite strength research available there exists a substantial amount of work related to the composite elastic modulus and the composite bulk modulus. The most interesting work stems from the mathematical analyses of particulate systems of Brandt (58) and Brown (59). This research has sought to compare concrete to particulate systems having full and zero continuity. Extensive mathematical models are presented and analyzed. However, none of this work appears to consider tensile forces and possible discontinuities. For a thorough detailing of the analyses of composites of a granular nature Deresiewicz (60) and Hashin (61) are recommended. From these two research results Brown (20) has suggested many limiting assumptions to make the analysis tractable. Consequently the resemblance of these particulate models to concrete is vague. Indeed Mather (62) doubts that even "Prepakt" concrete is a reasonable facsimile of the proposed model.

Hansen (63) has suggested that composites may be considered to be of two types:

1. high modulus matrix with low modulus particles and
2. low modulus matrix with high modulus particles.

Using Hashin's (62) generalized elastic modulus equation

$$\frac{E}{(1-2\nu)} = \left\{ \frac{(1-g)\frac{E_m}{1-2\nu_m} + \left(\frac{1+\nu_m}{2(1-2\nu_m)} + g\right)\frac{E_p}{1-2\nu_p}}{\left(1+\frac{1+\nu_m}{2(1-2\nu_m)}g\right)\frac{E_m}{1-2\nu_m} + \left(\frac{1+\nu_m}{2(1-2\nu_m)}(1-g)\right)\frac{E_p}{1-2\nu_p}} \right\} \frac{E_m}{1-2\nu_m} \cdots$$

where: ν = Poisson's ratio of the composite

ν_m = Poisson's ratio of the matrix

ν_p = Poisson's ratio of the particles

g = Fractional volume of particles

Hansen (63) has shown that when Poisson's ratios of -1.0 and +0.50 (64) are substituted in this equation the following equations result

$$\nu = -1.0; \quad E = (1-g)\,E_m + g\,E_p$$

$$\nu = +0.5; \quad E = 1\left[\left[(1-g)/E_m\right] + \left[g/E_p\right]\right]^{-1}$$

These are exactly the equations which would be expected for Hansen's type 1 and 2 composites respectively.

Upon analyzing several discrepancies between concrete and the various composite models Hansen (63) has suggested the practical formulae presented in Table AV.1. It should be realized that the formulae presented as a prediction for concrete strength and elastic modulus are for short term loading and make no allowance for time dependent effects.

AV.5 Summary and Discussion

Several approaches have been used in efforts to predict concrete strength and elastic modulus. All of these depend upon the theory of elasticity and the materials reaction to load on a phenomenological level as their basis. No theory appears to suitably represent the reaction of concrete to load at least under complex states of stress.

TABLE AV.1

Practical Formulae for Modulus of Elasticity of Concrete, Cement Mortar and Cement Paste (63)

Material	Matrix (m)	Particles (p)	Condition	Practical Formulae (E)
concrete	cement mortar	normal aggregate	$E_p > E_m$	$\dfrac{1}{\dfrac{(1-g)}{E_m} + \dfrac{g}{E_p}}$
concrete	cement mortar	lightweight aggregate	$E_p < E_m$	$\left(\dfrac{(1-g)E_m + (1+g)E_p}{(1+g)E_m + (1-g)E_p}\right)E_m$
concrete	concrete	voids caused by incomplete compaction	$E_p = 0$	$(1-g)^4 E_m$
cement mortar	cement paste	sand or aggregate	----	$0.5\left(\dfrac{1-g}{E_m} + \dfrac{g}{E_p}\right) + 0.5\left(\dfrac{1}{(1-g)E_m + gE_p}\right)$
cement paste	cement gel	capillary pores	$E_p = 0$	$\left(\dfrac{1-g}{1+2g}\right)E_m$
cement paste	cement paste	air-entrained pores	$E_p = 0$	$\left(\dfrac{1-g}{1+2g}\right)E_m$

(116)

There appears to have been a general disregard for the microstructural features in the theories presented to date, although a few authors make reference to Brunauer's (65) work (and the model of cement paste suggested therefrom). In the end, suitable formulations for the prediction of the reaction of concrete to load may be established only when significant experience has been accumulated for a given mix. At this time there does not seem to be any readily available reservoir of theory to allow the rational modelling of concrete systems.

REFERENCES FOR APPENDIX V

1. Feret, R., Studies on the internal constitution of hydraulic mortars, Bulletin de la Societe d'Encouragement pour l'Industrie Nationale, Vol. II, 1897, p. 1604.

2. Wischers, G., Effect of Temperature Variation on the Strength of Cement Stone and Mortar, Dusseldorf, Verein Deuscher Zementwerke, 1961, p. 117.

3. Powers, T.C., Physical Properties of Cement Paste, National Bureau of Standards Monograph No. 43, Vol. II Washington, 1962, pp. 577-609.

4. Abrams, D.A., Design of Concrete Mixtures, Chicago, Lewis Institute, Structural Materials Research Laboratory, Bulletin No. 1, Dec. 1918, p. 20.

5. Pickett, G., Effect of Aggregate on Shrinkage of Concrete and a Hypothesis Concerning Shrinkage, Journal of the Research and Development Laboratories (PCA), Vol. 1, No. 1, Jan. 1959, pp. 29-39.

6. L'Hermite, R., Volume Changes of Concrete, National Bureau of Standards, Monograph No. 43, Vol. II, Washington, 1962, pp. 659-694.

7. Ali, I. and Kesler, C.E., Creep in Concrete With and Without Exchange of Moisture with the Environment, University of Illinois, T. & A.M. Report No. 641, Dec. 1963.

8. Alexander, K.M. and Wardlow, S., Effect of Powdered Materials and Fine Aggregate in the Drying Shrinkage of Portland Cement Paste, Journal of the American Concrete Institute, Proceedings, Vol. 55, No. 12, June 1959, pp. 1303-1316.

9. Hansen, T.C. Theories of Multi-Phase Materials Applied to Concrete, Cement Mortar, and Cement Paste, The Structure of Concrete: Proceedings of an International Conference, London, Cement and Concrete Association, 1968, pp. 16-23.

10. Powers, T.C., Structure and Physical Properties of Hardened Portland Cement Paste, Journal of the American Ceramic Society, Vol. 41, No. 1, January 1958, pp. 1-6.

11. Neville, A.M., Creep of Concrete as a Function of Its Cement Paste Content, Magazine of Concrete Research, Vol. 16, No. 46, March 1964, pp. 21-30.

12. Arnstein, A. and Reiner, M., "Creep of Cement, Mortar and Concrete," Civil Engineering and Public Works Review, Vol. 40, Sept. 1945, pp. 198-202.

13. Glucklich, J. and Ishai, O., "Creep Mechanism in Cement Mortar," Journal of the American Concrete Institute, Proceedings, Vol. 50, No. 7, July 1962, pp. 923-948.

14. Dantu, P., "Study of the Stresses in Non-Homogeneous Materials and Its Application to Concrete," Annales de l'Institut Technique du Butiment et der Travaux Publics, Vol. 11, No. 121, January 1958, pp. 55-77.

15. Hansen, T.C., "Strength, Elasticity, and Creep as Related to the Internal Structure of Concrete," National Bureau of Standards, Monograph 43, Vol. II, Washington, 1962, pp. 709-723.

16. Hirsch, H.T., "Modulus of Elasticity of Concrete Affected by Elastic Moduli of Cement Paste Matrix and Aggregate," Journal of the American Concrete Institute, Proceedings, Vol. 59, No. 3, March 1962, pp. 427-452.

17. Dougill, J.W., "Discussion of paper by T.J. Hirsch," Journal of the American Concrete Institute, Proceedings, Vol. 59, No. 9, Sept. 1962, pp. 1363-1365.

18. Countu, V.J., "The Effect of the Elastic Modulus of the Aggregate on the Elastic Modulus, Creep, and Creep Recovery of Concrete," Magazine of Concrete Research, Vol. 16, No. 98, Sept. 1964, pp. 129-138.

19. Hansen, T.C., "Influence of Aggregate and Voids on Modulus of Elasticity of Concrete, Cement Mortar, and Cement Paste," Journal of the American Concrete Institute, Proceedings, Vol. 62, No. 2, Feb. 1962, pp. 193-216.

20. Brown, C.B., "Models for Concrete Stiffness with Full and Zero Contiguity," The Structure of Concrete: Proceedings of an International Conference, London, Sept. 1965, Cement and Concrete Association, Sept. 1968, pp. 3-15.

21. Anson, M., "An Investigation into a Hypothetical Information and Failure Mechanism for Concrete," Magazine of Concrete Research, Vol. 16, No. 47, June 1965, pp. 73-82.

22. Robinson, G.S., The Failure of Concrete with Particular Reference to the Biaxial Compressive Strength, Ph.D. Dissertation, Imperial College of Science and Technology, London, Nov. 1964.

23. Moavenzadeh, F., Kuguel, R., and Keat, L.B., Fracture of Concrete Research Report R68-5. Dept. of Civil Engineering, M.I.T., March 1968.

24. Brooks, A.E., and Newman, K., "The Structure of Concrete and Its Behavior Under Load," Proceedings of an International Conference, London, 1965, Cement and Concrete Association, London, 1968.

25. Newman, K., "The Structure and Properties of Concrete - An Introductory Review," The Structure of Concrete, Proceedings of an International Conference, London, 1968, pp. xiii-xxxii.

26. Cowan, H.J., "The Strength of Plain, Reinforced, and Prestressed Concrete Under the Action of Combined Stresses, with Particular Reference to the Combined Bonding and Torsion of Rectangular Sections," Magazine of Concrete Research, Vol. 5, No. 14, Dec. 1953, pp. 75-86.

27. Weibull, W., "A Statistical Theory of the Strength of Materials," Proceedings of the Royal Swedish Institute of Engineering Research, Stockholm, 1939, pp. 151.

28. Timoshenko, S., Strength of Materials, Part II, D. Van Nostrand, Princeton, 1956.

29. Timoshenko, S., History of the Strength of Materials, McGraw-Hill New York, 1953.

30. Guest, J.J., "On the Strength of Ductile Materials Under Combined Stress," Philosophical Magazine, Vol. 50, July 1900, pp. 69-132.

31. Nadai, A., Theory of Flaw and Fracture, McGraw-Hill, New York, 1950.

32. Timoshenko, S., Tessells, J.M., Applied Elasticity, Westinghouse Technical Night School Press, 1925.

33. Tettleman, A.S., and McEvily, A.J., Jr., Fracture of Structural Materials, John Wiley & Sons, Inc., New York, 1967.

34. Richart, F.E., Brandtzaeg, A., and Brown, R.L., "A Study of the Failure of Concrete Under Combined Compressive Stresses," University of Illinois Engineering Experimental Station, Bulletin No. 185, Vol. 26, 1928.

35. Balmer, G.G., "Shearing Strength of Concrete Under High Triaxial Stress-Computation of Mohr's Envelope as a Curve," Structural Research Lab. Report, S.P. No. 23, Bureau of Reclamation, U.S. Dept. of the Interior, 1949.

36. Bellamy, C.S., "Strength of Concrete Under Combined Stress," Journal of the American Concrete Institute, Proceedings, Vol. 5, No. 4, October 1961, pp. 367-381.

37. Wastlund, G., "Nya ron Angaende Betongens Grand laggande Halbfasthelsegenskaper," Betong (Stockholm), Vol. 3, 1937.

38. Weigler, H., Beker, G., "Untersuchungen uber dar Bruch-und Verfarnungsverhallen von Beton bei zweiachsiger Beanspruchung," Vertrieb Durch Verlag von Wilhelm, Ernest & Sohn, Berlin 1963.

39. Weigler, H., Becker, G., "Uber das Bauch-und Verfornumgsoer-halten von Beton bei mehrachsiger Beanspruchung," Der Bauingenieur Vol. 36, No. 10, October 1961, pp. 390-6.

40. McHenry, D., Karni, J., "Strength of Concrete Under Combined Tensile and Compressive Stress," Journal of the American Concrete Institute, Proceedings, Vol. 54, April 1958, pp. 829-40.

41. Bresker, B., Pister, R.S., "Strength of Concrete Under Combined Stresses," Journal of the American Concrete Institute, Vol. 30, No. 3., September 1958, p. 321.

42. Bresler, B., Pister, K.S., "Fracture of Plain Concrete Under Combined Stresses," Transactions of the American Society of Civil Engineers, Vol. 122, 1957, pp. 1049.

43. Tsuboi, Y., Suenaga, Y., "Experimental Study on Failure of Plain Concrete Under Combined Stresses," Part 3, University of Tokyo, Feb. 1960.

44. Bresler, B., Pister, K.S., "Strength of Concrete under Combined Stresses," Journal of the American Concrete Institute, Vol. 30, No. 3, Sept. 1958, p. 321.

45. Harris, A.J., "The Failure of Concrete Under Compound Stress," Symposium on the Strength of Concrete Structures, Cement and Concrete Association, London, 1956, pp. 201-18.

46. Brandtzaeg, A., "Failure of a Material Composed of Non-Isotropic Elements, An Analytical Study with Special Application to Concrete," Kgl. Narske Videnskab Selskabs Skrifter, No. 3, 1927, pp. 160-168.

47. Griffith, A.A., "The Theory of Rupture," Proceedings of the First International Congress for Applied Mechanics, Delft, 1924, pp. 55-63.

48. Inglis, C.E., Trans. Inst. of Naval Arch., London, Vol. 55, 1913, p. 219.

49. Irwin, G.R., "Fracture Dynamics" Fracturing of Metals, American Society of Metals, Cleveland, Ohio, 1948.

50. Westergaard, H.M., Journal of Applied Mechanics, Vol. 61A, 1939, p. 49.

51. Naus, D., Rejali, H.M., Lott, S.L., and Kesler, C.E., Cracking of Concrete, University of Illinois, Engineering Experiment Bulletin 504, 1970.

52. Kaplan, M.F., "Crack Propagation and the Fracture of Concrete," Journal of the American Concrete Institute, Proceedings, Vol. 58, No. 5, 1961, pp. 591-610.

53. Nakayama, T., "Direct Measurement of Fracture Energies of Brittle Heterogeneous Materials," Journal of the American Ceramic Society, Nov., 1965.

54. Lott, G.L., and Kesler, C.E., "Crack Propagation in Plain Concrete," University of Illinois, T.A.M. Report No. 648, 1964.

55. Glucklich, J., "On the Compression Failure of Plain Concrete," University of Illinois, T.A.M. Report No. 215, March 1962.

56. Glucklich, J., "The Flexural Static and Fatigue Failure of Portland Cement Mortar," University of Illinois, T.A.M. Report No. 622, 1962.

57. Ishai, O., "Influence of Sand Concentration on Deformation of Mortar Beams Under Low Stresses," Journal of the American Concrete Institute, Vol. 48, No. 5, Nov. 1961, pp. 611-623.

58. Brandt, H., "A Study of the Speed of Sound in Porous Granular Media," Journal of Applied Mechanics, Vol. 22, No. 4, Dec. 1955, pp. 479-486.

59. Brown, C.B., "Minimum Volumes to Ensure Homogeneity in Certain Conglomerates," Journal of the Franklin Institute, Vol. 279, No. 3, March 1965, pp. 189-199.

60. Deresiewicz, H., "Mechanics of Granular Matter," Advances in Applied Mechanics, Vol. 5, New York, Academic Press, 1958, pp. 233-306.

61. Hashin, Z., "Theory of Mechanical Behavior of Heterogeneous Media," Applied Mechanics Reviews, Vol. 17, No. 1, January 1964, pp. 1-9.

62. Mather, Bryant, Discussion of Reference (20), The Structure of Concrete, Proceedings of an International Conference, London, 1965, Cement and Concrete Association, 1968, p. 43.

63. Hansen, T.C., "Creep of Concrete - A Discussion of Some Fundamental Problems," Bulletin Swedish Cement and Concrete Research Institute, No. 33, Sept. 1958, pp. 1-48.

64. Webster, A.G., The Dynamics of Particles and of Rigid Elastic and Fluid Bodies, 3rd Edition, New York, Hafner Publishing Co., 1949.

65. Brunauer, S., "Tobermorite Gel--The Heart of Concrete," American Scientist, Vol. 50, No. 1, March, 1962, pp. 210-229.

APPENDIX VI

Details of Analytical Procedure for Five Micrometer Size Particles

AVI.1 General Procedure

In general the procedure was as follows:

1. disperse 17.0 grams of cement material in 500 grams of a solution consisting of $CaCl_2$ and 100% ethyl alcohol.
2. allow the cement particles to settle,
3. pipette off the supernatant fluid containing the -5 micrometer particles,
4. pipette off a sample of the coarser material lying at the bottom of the settling cylinder,
5. evaporate to dryness the pipetted material under an infrared lamp, and
6. analyze the residue for SO_4^{-2}.

AVI.2 Details of Procedure

AVI.2.1 Preparation of $CaCl_2$--Ethyl Alcohol Solution

Sixty grams of $CaCl_2$ were added to a 1000 ml volumetric flask. To this was added 100% ethyl alcohol to make a total volume of 1000 ml. The viscosity of this solution was determined using a falling ball viscometer. The average viscosity of the solution was 1.18 centipoises at 23 C.

AVI.2.2 Preparation of Cement Suspension

In a dispersion cup 17.0 grams of cement were mixed with 500 ml of the $CaCl_2$--alcohol solution. This was mechanically blended in a Hamilton-Beach "milk shake mixer" for two minutes. Immediately after mixing, the contents of the cup were poured into a 500 ml graduated cylinder. Some residue was observed in the bottom of the dispersion

cup. Assuming that this material was grossly larger than five micrometers, it was not added to the graduated, settling cylinder.

AVI.2.3 Isolation of a Five Micrometer Size Fraction

Using Stokes law as suggested by Grindrod (67) it was determined that the supernatant liquid in the top 5.5 cm of the settling column (approximately 100 ml) should contain either -5.0 or -6.2 micrometer material after 34 minutes of settling depending upon whether the specific gravity of cement, 3.15, or gypsum, 2.72, was used in the Stokes settling equation respectively. In all cases reported herein a time of settling of 34 minutes was used.

AVI.2.4 Separation of Samples

Using a pipette 100 ml of the supernatant suspension was removed to a drying beaker from the settling cylinder after 34 minutes. The pipette was never more than 5 mm from the falling surface of the liquid. A comparison sample of 100 ml was pipetted from the residue settled at the bottom of the cylinder.

AVI.3 Determination of SO_4^{-2} Content

The material removed from the settling cylinder was removed to a clean, preweighed drying flasks. The ethyl alcohol was evaporated using an infrared lamp. The residue in the beaker was analyzed for SO_4^{-2} using a $BaCl_2$--precipitation technique.

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